STABILISATION OF DIAZO COMPOUNDS USED IN LITHOGRAPHIC SYSTEMS

by

RICHARD HERSEY MSc, BSc, C. Chem., MRSC

A thesis submitted to the Council of National Academic Awards in partial fulfilment of the requirements for the degree of Doctor of Philosophy

APRIL 1991

Sponsoring establishment : Sheffield City Polytechnic
School of Science, Division of Chemistry
Collaborating establishment : DuPont Howson
Research Laboratories

ABSTRACT

Stabilisation of diazo compounds used in lithographic systems

by Richard Hersey

The research undertaken has been an investigation of the deterioration that occurs during lithographic plate manufacture and storage. The aim of the research was to identify and eliminate the causes of the deterioration.

Deterioration was found to be due to the presence in the formulation of diazonium compounds that were thermally unstable. These compounds were studied in coating solutions and printing plates.

Alternative analytical techniques for diazonium analysis were examined. It was found that HPLC and UV/vis spectroscopy were most useful. These techniques gave information on loss of specific diazonium compounds or loss of diazonium character respectively.

Identification of the decomposition products and an assessment of the components of the matrix that influenced the rate of decomposition provided information on the decomposition mechanism. This was found to be largely free radical based and hence accelerated by the presence of electron donating solvents.

Several diazonium salts were examined notably to determine what substituents influenced the rate of decomposition. Ortho and para electron donating substituents improved stability. The counterion used also had an influence on diazonium stability. Tetrafluoroborate salts were found to be more stable than hexafluorophosphates. Diazonium salts with other counterions were also prepared and the short chain alkyl sulphonates were particularly stable.

Additives and stabilisers were assessed but only the use of crown ethers and high molecular weight polyethers gave a significant diazonium stability improvement.

A comparison was made between the effects of photolytic and thermal decomposition. Fortunately, compounds that are thermally stable react readily to light, resulting in good lithographic properties. This was explained as being due to a heterolytic mechanism predominating for photolytic reaction compared to a homolytic mechanism for thermolysis.

CONTENTS

ABSTRACT 2

STRUCTURES 6

REACTION SCHEMES 8

FIGURES 10

TABLES 12

ACKNOWLEDGEMENTS 14

1 INTRODUCTION 15
1.1 SAFETY CONSIDERATIONS 16
1.2 COMMERCIAL IMPLICATIONS 18
1.3 LITHOGRAPHIC PRINTING 19
1.4 POSITIVE PLATES 21
1.5 NEGATIVE PLATES 24
1.6 POSITIVE PLATE CHEMISTRY 26
1.7 NEGATIVE PLATE CHEMISTRY 28
1.8 REVIEW OF DIAZONIUM SALT DECOMPOSITION REACTIONS 31
1.8.1 The Balz-Schiemann Reaction 31
1.8.2 Diazonium salt structure 35
1.8.3 Decomposition Investigations 39
1.8.4 Stabilised diazo compounds 50
1.9 INVESTIGATIVE STRATEGY 56

2 RESULTS AND DISCUSSION 58
2.1 INITIAL INVESTIGATIONS 58
2.2 PRELIMINARY EXPERIMENTS ON DIAZONIUM SALT COATINGS 65
2.2.1 Factors affecting decomposition rate: cresols and novolaks 65
2.2.2 Time and temperature effects 77
2.2.3 Solvent and Water effects 81
2.2.4 Concentration Effects 87

2.3 ANALYSIS OF DECOMPOSITION PRODUCTS 89
2.3.1 Introduction 89
2.3.2 Products detected in full plate formulations 91
2.3.3 Counter-ion decomposition products . 96
2.3.4 Detection of oligomeric products . 101
2.3.5 Decomposition Mechanism 106
2.4 METHODS OF ANALYSIS OF AROMATIC DIAZONIUM SALTS 109
2.4.1 Chemical Methods 109
2.4.2 Polarographic Methods 112
2.4.3 Chromatographic Methods 113
2.4.4 Spectroscopic Methods 114
2.4.5 Analysis techniques conclusion . . 118
2.5 ALTERNATIVE DIAZONIUM SALTS AND COUNTERIONS 120
2.5.1 Alternative Diazonium salts 120
2.5.2 Alternative Counterions 131
2.6 STABILISATION BY ALTERNATIVE SOLVENTS AND ADDITIVES 135
2.6.1 Alternative Solvents 136
2.6.2 Addition of stabilisers 140
2.7 HOST-GUEST COMPLEXATION 143
2.7.1 Effect of crown ethers in lithographic systems 144
2.7.2 Effects of other polyethers 147
2.8 POLYMERIC DIAZONIUM SYSTEMS 148
2.9 DIAZONIUM STABILITY ON PLATES 150
2.9.1 Positive Plates 150
2.9.2 Negative Plates 151
2.10 PHOTOLYSIS VS. THERMOLYSIS 153
2.11 CONCLUSIONS 156

3 EXPERIMENTAL DETAILS 158
3.1 SAFELIGHT REQUIREMENTS 158
3.2 SOLIDS CONTENTS OF COATING SOLUTIONS . . . 158
3.3 PLATE COATING WEIGHT 159
3.4 HPLC METHOD FOR 2,1,5 NAPHTHOQUINONE DIAZO ESTER OF 2,4 DIHYDROXYBENZOPHENONE . . . 160

3.5 HPLC METHOD FOR COLOUR CHANGE DYES IN COATINGS 163
3.6 HPLC ANALYSIS OF DIAZODIPHENYLAMINE SALTS 164
3.7 WATER CONTENTS BY KARL FISCHER (INCLUDING KETONES) 166
3.8 HEXAFLUOROPHOSPHATE AND TETRAFLUOROBORATE BY ION CHROMATOGRAPHY 167
3.9 GAS CHROMATOGRAPHY / MASS SPECTROMETRY OF POSITIVE PLATE COMPONENTS 170
3.10 PREPARATION OF EXPERIMENTAL TEST PLATES . 172
3.11 GEL PERMEATION CHROMATOGRAPHY 173
3.12 INFRA-RED SPECTROSCOPY 176
3.13 THERMAL ANALYSIS 176
3.14 HYDROXY VALUE OF NOVOLAKS 177
3.15 ULTRA-VIOLET/VISIBLE SPECTROSCOPY OF DIAZONIUM SALTS 177
3.16 PULSED SQUARE WAVE VOLTAMETRY 177
3.17 ION-EXCHANGE OF THE DIAZONIUM COUNTERION 178

4 REFERENCES 180

STRUCTURES

1: Arenediazonium cation 15
2,3: Mesomeric structures for diazo derivatives of ortho and para aminophenol 16
4: 4,6 Dinitrobenzoquinone-2-diazide 17
5: Oxirane 23
6: Cresol novolak 26
7: Quinonediazide sulphonic acid chloride 27
8: Generalised epoxy resin structure 28
9: Diazodiphenylamine/formaldehyde condensation polymer 31
10,11: Quinoid structures of diphenylquinomethane and the p-amino aryl diazonium ion 36
12: Charge transfer from the diazonium group to the amino 38
13: Resonance form of the p-nitrobenzenediazonium ion 47
14: Host-guest complexation of diazonium by 18-crown-6 cyclic ether 53
15: Reduced complexation of anilinium cation 54
16: Mono and bis 1,2-naphthoquinone diazide-5-sulphonic acid esters of 2,4-dihydroxybenzophenone 59
17: Diazodiphenylamine tetrafluoroborate 60
18: Generalised structure for acid/base azo dye . . . 60
19: Diphenylamine/m-cresol product 104
20: Diphenyl benzidine 104
21: Coupled diazodiphenylamine products 105
22: Diacetone alcohol 107
23: Diphenylamine-4-diazonium tetrafluoroborate . . 121
24: Diphenylamine-4-diazonium hexafluorophosphate . 121
25: 2-Methoxy-diphenylamine diazonium tetrafluoroborate 121
26: 2,5 Diethoxy-4'-methyl-diphenylsulphide 4-diazonium tetrafluoroborate 121
27: 2,5 Diethoxy-4'-methyl-diphenylsulphide 4-diazonium hexafluorophosphate 121
28: 2,5 Diethoxy-4-morpholino diazonium tetrafluoroborate 121

29: 2,5 Dipropoxy-4-morpholino diazonium hexafluorophosphate 121
30: 2,5 Dibutoxy-4-morpholino diazonium hexafluorophosphate 121
31: 3-Chloro-4-dimethylamino diazonium hexafluorophosphate 122
32: 3-Chloro-4-pyrrolidinobenzene diazonium hexafluorophosphate 122
33: 3-Chloro-4-hexamethyleneiminobenzene diazonium hexafluorophosphate 122
34: 3-Chloro-4-cyclohexyl-methylaminobenzene diazonium hexafluorophosphate 122
35: 2-Chloro-4-diethylamino-5-p-chlorophenoxybenzene tetrafluoroborate 122
36: Dibenzylphosphoric acid 133
37: Diphenylphosphinic acid 133
38: Diphenylphosphoric acid 133
39: Tinuvin 292 141
40: Tinuvin 328 141
41: Tinuvin P 141
42:Theophylline stabilisers 142

REACTION SCHEMES

Scheme 1: The reaction of 1,2 quinone-2-diazide to light 22
Scheme 2: Photolysis of 1,2 naphthoquinone 2- and 1-diazides 23
Scheme 3: Use of C^{13} labelling in 1,2 naphthoquinonediazide studies 23
Scheme 4: Decarboxylation of indene carboxylic acid . 27
Scheme 5: Photolytic decomposition of diazonium salt 28
Scheme 6: Cationic polymerisation of epoxides 29
Scheme 7: Formation of Lewis acids during photolysis of diazonium salts 29
Scheme 8: Conversion of aromatic amines to the fluoride via the Balz-Schiemann reaction . 32
Scheme 9: Postulated reaction mechanisms for the Balz-Schiemann) 33
Scheme 10: Use of hexafluorophosphate in the Balz-Schiemann reaction 34
Scheme 11: Canonical forms of the diazonium salt . . 35
Scheme 12: Cationic(A) and radical(B) mechanisms for diazonium decomposition 40
Scheme 13: Formation of polymeric products from radical dediazoniation 41
Scheme 14: Reversible dediazoniation via a molecular-ion pair intermediate 42
Scheme 15: Radical mechanism for hydro-dediazoniation in methanol in the absence of oxygen 43
Scheme 16: Formation of stable entities from radical dediazoniation 43
Scheme 17: Colour change reaction with Lewis acid . . 60
Scheme 18: Reaction between dimethoxy propane and water 84
Scheme 19: Reversible reaction between molecular nitrogen and an aromatic cation 86
Scheme 20: Reaction of ion-molecule pair with water . 87
Scheme 21: Complex formation between Lewis acid and aromatic amine 100

Scheme 22: Cationic mechanism for diazonium decomposition 107
Scheme 23: Radical reaction mechanism for diazonium decomposition 108
Scheme 24: Titrimetric assay of diazonium salt . . 110
Scheme 25: Coupling reaction for diazonium determination 110
Scheme 26: Reduction reaction of arenediazonium salts 112
Scheme 27: Reduction reaction of diazonium salts in aprotic solvents 129
Scheme 28: Karl Fischer reaction 166
Scheme 29: Reaction of ketones to give water . . . 167

FIGURES

Figure 1: The exposure and development of a positive working lithographic plate. 21
Figure 2: The exposure and development of a negative working lithographic plate. 25
Figure 3: Ultra-violet spectra of a diazo ester and diazodiphenylamine salt. 64
Figure 4: Gel permeation chromatogram of cresol novolak resin using two PLGEL mixed pore size columns. 72
Figure 5: Gel permeation chromatogram of the high molecular weight cresol novolak fraction. . . . 74
Figure 6: Gel permeation chromatogram of the medium molecular weight cresol novolak fraction. . . . 75
Figure 7: Gel permeation chromatogram of the low molecular weight cresol novolak fraction. . . . 76
Figure 8: Diazodiphenylamine tetrafluoroborate stability in 10 %w/v cresol and cresol novolak solutions in acetone stored at 40 °C. 78
Figure 9: The effect of temperature on the rate of diazodiphenylamine decomposition in 10 %w/v pyrogallol in acetone solution. 80
Figure 10: Partial ion chromatogram of an acetone extract of a baked plate after 24 hours at 105°C. 92
Figure 11: Partial ion chromatogram of an unbaked plate. 93
Figure 12: Thermally desorbed positive plate total ion chromatogram. Mass spectra taken at points indicated. 94
Figure 13: Selective ion monitoring at 169 and 187 Daltons of a thermally desorbed diazodiphenylamine decomposition product from a positive plate. 95
Figure 14: Comparative decompositions of diazonium and tetrafluoroborate in 10 % cresol solution. . 98
Figure 15: Comparative decompositions of diazonium and hexafluorophosphate in 10 % cresol solution. 99

Figure 16: Gel permeation chromatogram of 42 % decomposed diazodiphenylamine in 10 % w/v m-cresol. 102
Figure 17: Mass spectrum of the high molecular weight fraction from a diazodiphenylamine decomposition. 103
Figure 18: Infra-red spectrum of diazodiphenylamine hexafluorophosphate (KBr disc) 117
Figure 19: Infra-red spectrum of diazodiphenylamine hexafluorophosphate in 10 % m-cresol in acetone after subtraction of the cresol solution spectrum. 119
Figure 20: Thermogram of Structure 25 125
Figure 21: Thermogram of structure 33 126
Figure 22: Reduction profile of a diazonium salt using pulsed square wave voltammetry and a gold electrode. 130
Figure 23: Effect of 18-crown-6 ether concentration on diazonium stability and the shift in the position of the uv absorption maximum. 146
Figure 24: Superimposed reflectance UV/visible spectra during aging of a plate coated with a diazonium polymer. 152
Figure 25: Chromatogram of exposed diazodiphenylamine in acetone solution after complete decomposition 154
Figure 26: Mass spectrum of the major photolysis degradation product of diazodiphenylamine in acetone 155
Figure 27: Separation by ion chromatography of common anions. 168
Figure 28: Ion chromatography anion micro-membrane suppressor. 169
Figure 29: Gel permeation chromatography calibration using polystyrene molecular weight standards, corrected using a toluene retention marker. 175

TABLES

Table 1: Values of σ^- for para substituents 45
Table 2 : Plate analyses after 7 days storage at 5, 30 and 40 °C 62
Table 3 : Coating analyses after 7 days storage at 5, 30 and 40 °C 62
Table 4 : Diazodiphenylamine decompositions after 6 days storage at 40 °C in 10% w/v solutions of various alkylhydroxybenzenes 67
Table 5: Mixture of alkylhydroxybenzenes used in the manufacture of cresol novolak (results as supplied by the manufacturers) 68
Table 6: Phenolic monomers measured by gas chromatography in cresol novolak resins 68
Table 7 : Diazodiphenylamine decomposition levels measured after 7 days at 40 °C in 10% w/v solutions of commercial phenol and cresol formaldehyde condensates (novolaks) 70
Table 8: Cresol Novolak molecular weight fractionation results 73
Table 9: Effects of novolak fractions on diazodiphenylamine salt decomposition 75
Table 10 : The effects of temperature and time on diazodiphenylamine decomposition rate in 10% w/v pyrogallol in acetone 79
Table 11 : The relative decompositions of diazodiphenylamine in a range of ketonic solvents containing 10% w/v pyrogallol 81
Table 12 : The effect of water on the decomposition rate of diazodiphenylamine in acetone containing 10% w/v pyrogallol 82
Table 13: The effects of relative concentration of diazodiphenylamine and pyrogallol on the decomposition rate of diazodiphenylamine 88
Table 14: Percentages of decomposition products formed during diazodiphenylamine salt decomposition in m-cresol solution. 105

Table 15: Comparison between HPLC and UV/vis measurement of diazonium salt percentage decomposition 116
Table 16: Thermal analysis results for various diazonium salts 124
Table 17: Stability and λ max. for diazonium salts 126
Table 18: Stability and half-wave potentials for a range of diazonium salts 130
Table 19: Stabilities of diazodiphenylamine salts having a range of different counterions . . . 134
Table 20: Conductivity measurements in μS/cm.of diazodiphenylamine hexafluorophosphate in various solvents at different concentrations (in gm/100ml) 137
Table 21: Stability comparisons for diazonium in various solvents and in cresol novolak solution compared to conductivity 138
Table 22: Crown ether stabilisation of diazodiphenylamine 145
Table 23: Diazonium stability comparisons in the presence of polyethylene glycols and 18-crown-6 ether 148
Table 24: Effect on molecular weight of diazonium polymer after 2 days at 40 °C in acetone solution 150
Table 25: Factors affecting diazonium salt stability 157

ACKNOWLEDGEMENTS

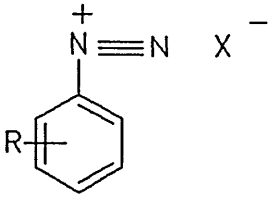
I wish to acknowledge the constructive guidance of Dr. David Leathard (Director of Studies) and Prof. David Allen (Second Supervisor) throughout the work on this project. Their comments and persistence helped make sure I completed the work within a reasonable time and to a good standard.

Thanks are also due to various colleagues at Du Pont Howson. These are to Dr. John Evans for agreeing to the sponsorship, to Dr. Rod Potts for agreeing to act as my supervisor at Du Pont Howson, and to Keith Hargreaves and members of the Analytical Department for assistance with the analysis.

1 INTRODUCTION

This thesis describes the work undertaken to solve a major practical problem in lithographic printing; the limited shelf life of the printing plate product. It reports an investigation into the factors governing the decomposition mechanisms of certain diazo compounds.

The name diazo or diazo compound is used as a generic name including all forms in which these compounds exist. The term diazonium is restricted to diazo compounds in the form of salt-like cations. This investigation covers aromatic diazo compounds only. The ground state of arenediazonium cations is generally represented by structure (1), where X^- may be a simple inorganic or complex inorganic or organic anion.

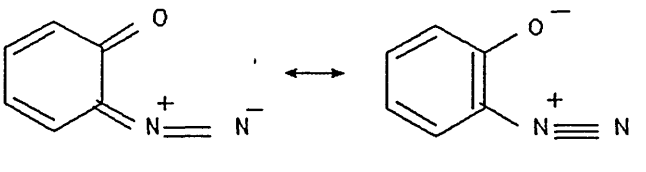


(1: Arenediazonium cation)

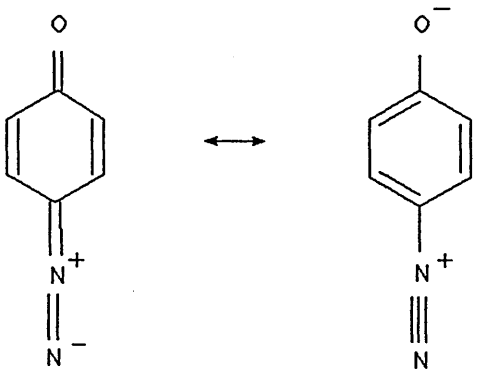
The other major class of diazo compounds which will be encountered are the quinonediazides. These are prepared by diazotisation of an arylamine having a hydroxy group ortho or para to the amino group. They have properties quite different from those of a typical diazonium salt. Their structures are best represented as mesomeric systems in which the limiting forms are the quinonediazides and the diazophenol zwitterions. Thus o-aminophenol yields the system 2a and 2b and p-aminophenol the system 3a and 3b.

There is no requirement for an external anion to counter the charge distribution in the quinonediazides. The influence of substituents and chemical structure on the properties of the diazo group will be considered in greater detail in a later section.

Diazo-containing chemical compounds find extensive application in the printing and printed circuit board



(2a) (2b)



(3a) (3b)

(2,3: Mesomeric structures for diazo derivatives of ortho and para aminophenol)

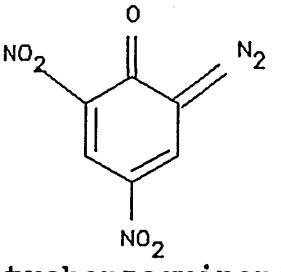
industries as well as in the manufacture of dyestuffs. The diazo compounds of interest in this thesis are those that find use in the lithographic printing industry as a result of their high photochemical reactivity. Such compounds are by their very nature designed so as to react with minimal exposure to light and are therefore inherently unstable.

Diazo compounds are also extremely thermally unstable. This results in two major problems: safe handling during the preparation of the diazo compounds, and plate product deterioration either during manufacture or before the plate is used by the customer.

1.1 SAFETY CONSIDERATIONS

The well-known instability of diazo compounds is one of their outstanding characteristics. In a modern industrial chemical plant the processes used have been developed based upon over a century of the sometimes hard won experience of earlier chemists. Relatively stable diazo compounds are used that are more problematical

because of their limiting effect on product lifetime than through any explosive danger. Nevertheless the greatest care should be taken in the handling of diazo salts in the solid form, even if damp, but especially when dry or after storage. New diazonium salts should be assumed to be dangerous, and until their properties have been established by systematic hazard tests the mass of specimens should be restricted to a few grams. References to damage caused by explosions are found in the literature from the first paper published by Griess[1] onwards. He wrote in 1858 of 4,6-dinitrobenzoquinone -2- diazide (4). "This substance cannot endure the heat of a water-bath but is decomposed by it with a violent explosion."



(4: 4,6 Dinitrobenzoquinone-2-diazide)

Diazonium salts have caused similar problems to the quinonediazide mentioned above. Both the nature of the diazonium cation and the anion associated with it influence the possible hazard. The chloride and sulphate generally are less dangerous than the nitrate. Griess again in 1867[2] recorded a "fearful explosion" initiated by benzenediazonium nitrate, and the introduction of a nitro group into the nucleus was found to increase explosiveness. Bamberger in 1895[3] experienced a severe explosion of p-nitrobenzenediazonium nitrate. As a general rule the greater the relative molecular mass of a diazonium compound, the greater is its stability. Diazonium salts of low molecular mass are liable to explode even when damp. A violent explosion of a small sample of 5-phenyl-1,2,4-triazole-3-diazonium sulphate has been recorded[4] . It is noteworthy that the same chemist had previously prepared the same compound several times without mishap. After a serious explosion in 1969 during

the diazotisation of 1200 mole of 6-chloro-2,4-dinitroaniline when three workmen were killed, a study of the sensitivity of diazo compounds to heat and shock was carried out, using the techniques of explosives technology, and safety measures for industrial diazotisation were recommended[5].

1.2 COMMERCIAL IMPLICATIONS

Apart from the overriding safety consideration, the photochemical and thermal sensitivity of diazo compounds results in other problems in an industrial context. Diazo compounds must be handled under safelight conditions and not subjected to elevated temperatures for any length of time. In the lithographic printing industry this entails restrictions on the lighting conditions during plate manufacture. Similarly while dissolution of coating chemicals is taking place during plate coating preparation, care must be taken to ensure that any temperature rise due to shear effects is kept to a minimum. Nevertheless, coating solutions typically require about 6 hours to dissolve the resins used. Analysis and adjustments of coatings to give the correct formulation, result in a delay of up to two days. During this time the coating will be stirred continuously. After filtering the solution will be ready for coating preparation. One batch of coating can be used for two weeks continuous production. Throughout this period it will be maintained at a slightly elevated temperature of about 30 °C so as to give correct flow properties and a satisfactory final plate appearance. This length of time at above ambient temperatures has profound implications for satisfactory production in view of the instability of the diazo compounds.

Printing plates are exported all over the world. This results in storage during transit and at the customers' premises for several months before use. Temperatures as high as 35-45 °C may be encountered in

some hotter countries. Although a shelf life of up to one year can be achieved for some diazo-containing plates, this is only possible in temperate climates. Shelf-life is severely curtailed in warmer countries. Plate stability problems result in usable shelf lives of only a few months under poor storage conditions.There are correspondingly increased complaints from customers concerning deterioration in plate performance, not only from hot countries but also from deterioration in transit through these warmer climates.

This investigation was undertaken with the practical aim of extending the shelf life of lithographic printing plates through an understanding of the processes involved.

To put the role of the diazo compounds into context it is first necessary to explain the fundamentals of printing plate chemistry.

1.3 LITHOGRAPHIC PRINTING

Photolithography is the process of printing from specially prepared surfaces, some areas of which are capable of accepting lithographic ink, whereas other areas, when moistened with water, will not accept ink. The areas which will accept ink form the printed image, and the ink-rejecting areas form the background.

Photolithography is a planographic process, which means that the printing and non-printing sections are at the same level. The coating is only 1-2 microns thick. This is in contrast to flexography and some out-dated etching printing processes where the physical difference in height of image and background areas largely determined whether ink would be taken up or not. Therefore the object of lithographic plate making is to form on a plate an image or design that will be ink-receptive and chemically different from the background areas. In addition the background areas must be of a type to take water and repel ink.

Photolithographic printing plates are usually made of aluminium. The plates must be thin and flexible enough to wrap snugly round the printing cylinder. The thickness varies according to press size from 0.15 to 0.50 mm.

The initial step in the preparation of the surface of lithographic plates is the graining operation, giving the surface of the metal a uniform rough texture consisting of microscopic hills and valleys, which serve as storage places for water in background areas and as anchorage centres for the image. Graining was formerly a mechanical operation using abrasives suspended in water but is now more usually carried out in an electrochemical acid bath.

After graining, continuous production of lithographic plates from an aluminium web necessitates an anodising stage. This is a further electrochemical process whereby the metal becomes the anode in an electrochemical cell. This results in a smooth oxide film which considerably increases the available surface area and improves the adherence of organic chemicals.

The chemical coating is applied from a coating bath to the grained and anodised aluminium surface. This is a photosensitive blend of chemicals in an organic solvent which is dried off to give a coating of about 1-2 g/m^2.

Printing plates can operate in either of two contrasting ways. These are called POSITIVE and NEGATIVE working plates. As might be inferred from the names, these utilise chemical processes that result in opposite configurations of image to non-image areas. Both plate types are exposed through a film in contact with the plate: vacuum is applied to ensure good contact between the film and plate. The light source is a mercury discharge lamp. A sheet of glass that is incorporated in the exposure frame maintains the vacuum contact and has the effect from a technical point of view of absorbing some of the lower wavelength emissions of the lamp. The differences in the two plate types explained below are clarified in Figures 1 and 2.

1.4 POSITIVE PLATES

As shown in Figure 1: the film used for the exposure is a positive of the required final copy; that is to say on the film, print is black and the surrounding background clear. On exposure, light only impacts on the none image areas. The photosensitive coating typically comprises a mixture of an alkali soluble resin and a developer inhibitor, usually an o-quinonediazide.

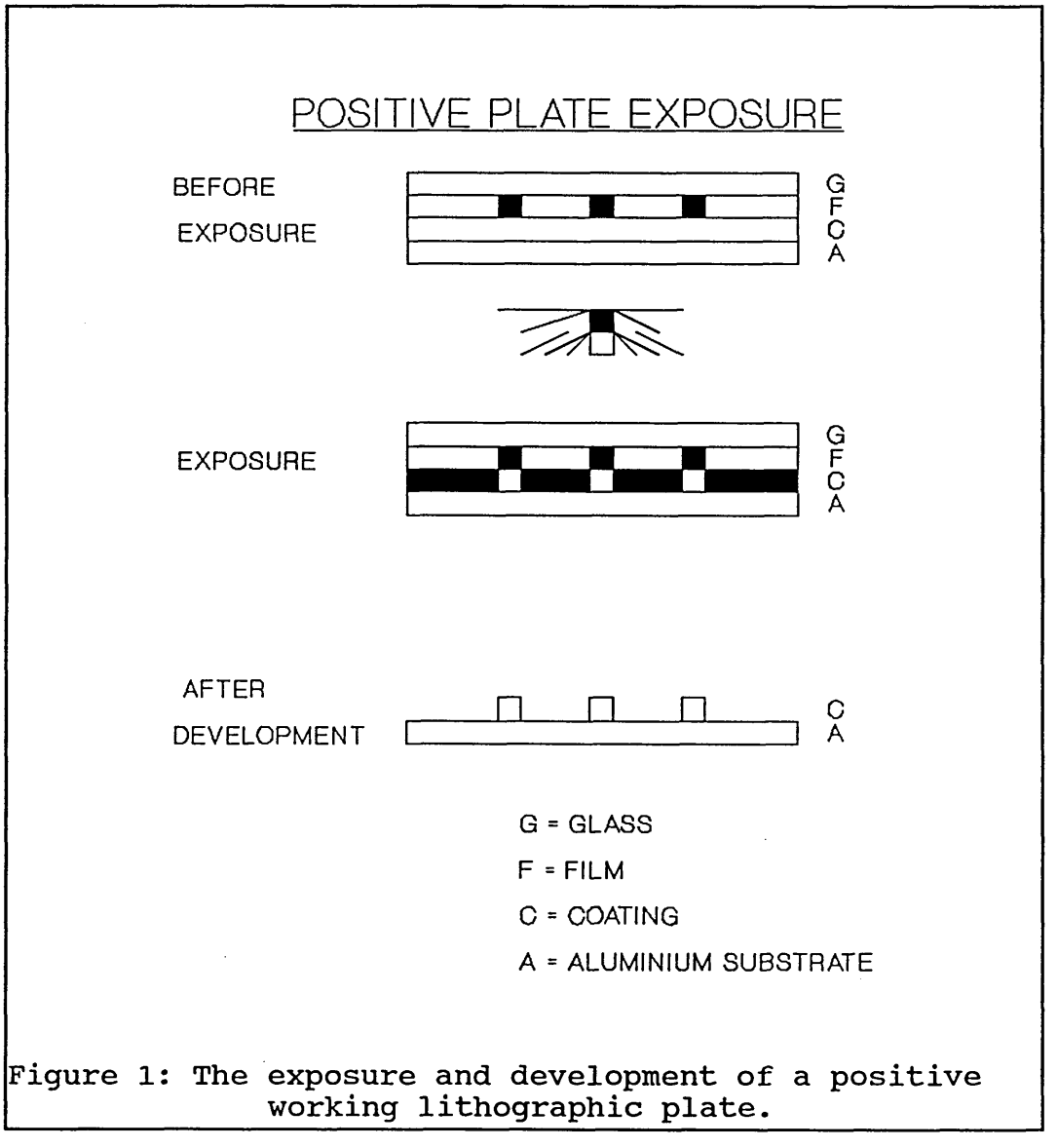
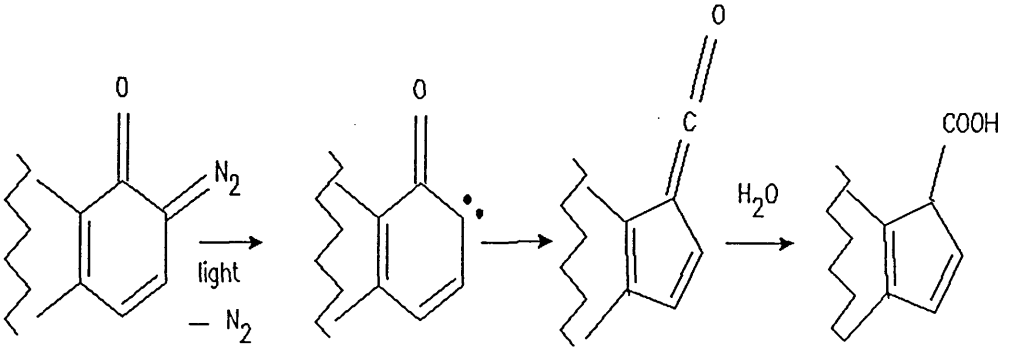


Figure 1: The exposure and development of a positive working lithographic plate.

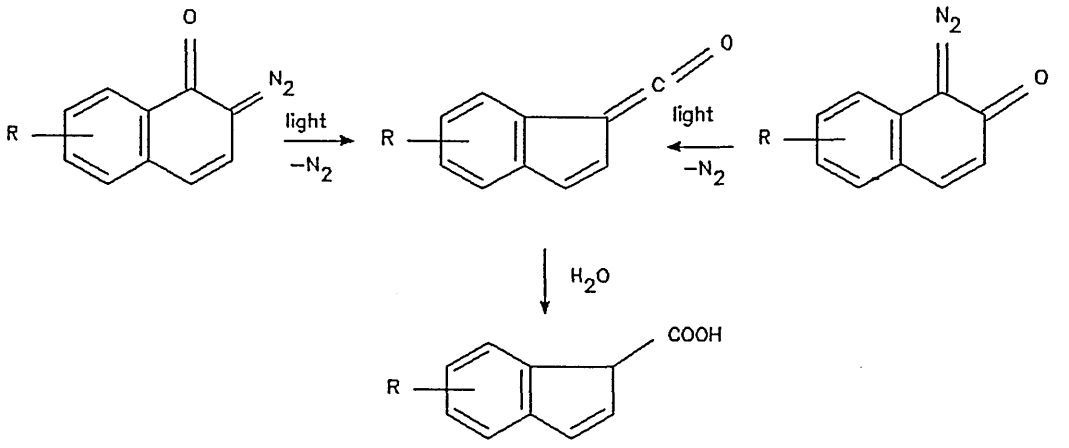
The o-quinonediazides of the naphthalene series are most important in this application; they are initially ink receptive and after exposure can be dissolved out by aqueous alkaline developers. The unexposed parts retain

their oleophilic properties. The chemical changes taking place during exposure are due to the closeness of the diazo and carbonyl groups. In these terms the 1,2 quinonediazides can be considered as a specific type of alpha diazoketone. There is much in common in the chemical behaviour of 1,2 quinonediazides and similar aliphatic alpha diazoketones. This appears particularly in their thermal and photochemical reactions. In both cases carbene systems are formed as intermediates. The carbonyl group and the ketene are adjacent to one another and this gives rise to their specific behaviour which contrasts with that of other diazo derivatives. Such α-ketocarbene systems are inclined to isomerism. This reaction was first discovered in 1902 by Wolff for α-diazoketones[6]. In this case reaction proceeds via a carbene intermediate which rearranges to give a ketene, which in the case of 1,2 quinonediazides reacts further with water to give an indene carboxylic acid (Scheme 1). The diazoketone evolves a molecule of nitrogen producing the ketocarbene. Subsequently the ketocarbene skeleton rearranges to give the corresponding ketene. Addition of water, alcohol or amine to the ketene gives either the acid or its derivative. This reaction and others of the same type was first investigated in detail by Sus[7-9].



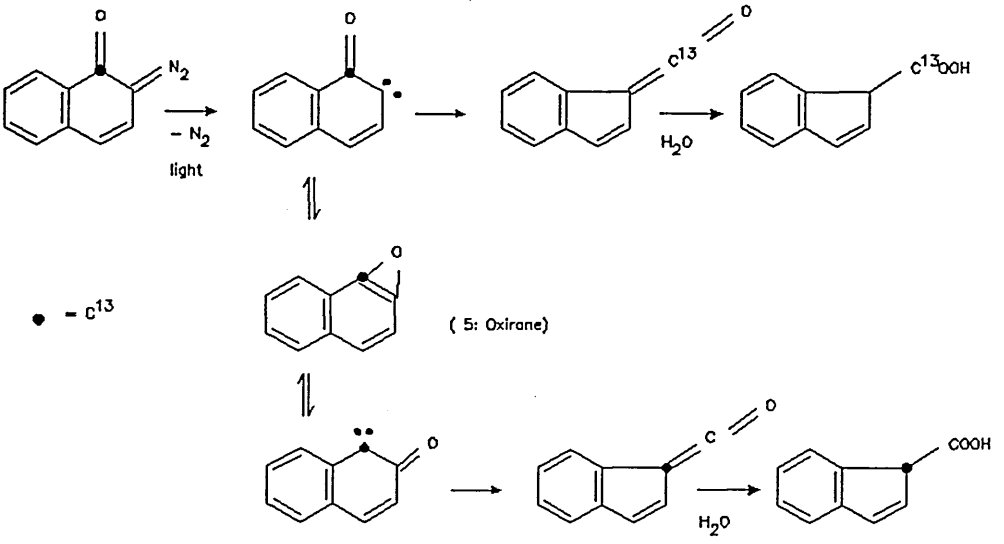
(Scheme 1: The reaction of 1,2 quinone-2-diazide to light)

The photolysis of isomeric 1,2-naphthoquinone 2- and 1-diazides results in the formation of the same products (Scheme 2).



(Scheme 2: Photolysis of 1,2 naphthoquinone 2- and 1-diazides)

A study of this reaction with labelled compounds by Zeller [10] has shown that the appearance of the same indenecarboxylic acids cannot be explained by the oxirane-ketocarboxylic rearrangement (Scheme 3 below).



(Scheme 3: Use of C^{13} labelling in 1,2 naphthoquinonediazide studies)

He used a C^{13} isotope labelled 1-carbon atom and thus determined whether the carboxylic acid group is derived from it or from the 2-carbon atom in accordance with the

first or second routes shown. The finding of all the C^{13} in the carboxylic acid group proved that the reaction does not follow the second route via the oxirane (5). It is due to the formation of indenecarboxylic acid that the areas exposed to light can be removed with alkaline developer solution. Thus a chemical change has occurred in the areas which have been exposed to light that renders them comparatively easy to remove by developer. The unexposed areas remain on the plate and when a solution of ink/water is applied, the ink adheres to the oleophilic unexposed areas and is repelled from the areas from which the organic chemical coating has been removed. This process results in a positive print of the original copy.

1.5 NEGATIVE PLATES

The processing of negative plates is, as might be expected, the reverse of that for positive ones. As illustrated in Figure 2, a film of the copy to be reproduced is again used in vacuum contact with the printing plate but this time the film is a negative of the required final printed material. The characters and other copy to be printed are clear and the background is opaque. Light passing through the clear areas impacts on a mixture of photosensitive resins, initiators and sensitisers which causes the resins to crosslink and harden on exposure. When treated with a developer solution, the exposed crosslinked areas are unaffected but the unexposed coating is developer soluble and is removed. This results in a final plate that is visually identical to the positive plate after exposure and development. The characters to be printed are coating chemicals which are oleophilic. When treated with the ink/water mix by the printer the characters to be printed will take ink but the background area of anodised aluminium will repel ink.

Why are there the two types of plate? The positive plates are easier to check for plate defects during plate/film exposure and development as they are identical

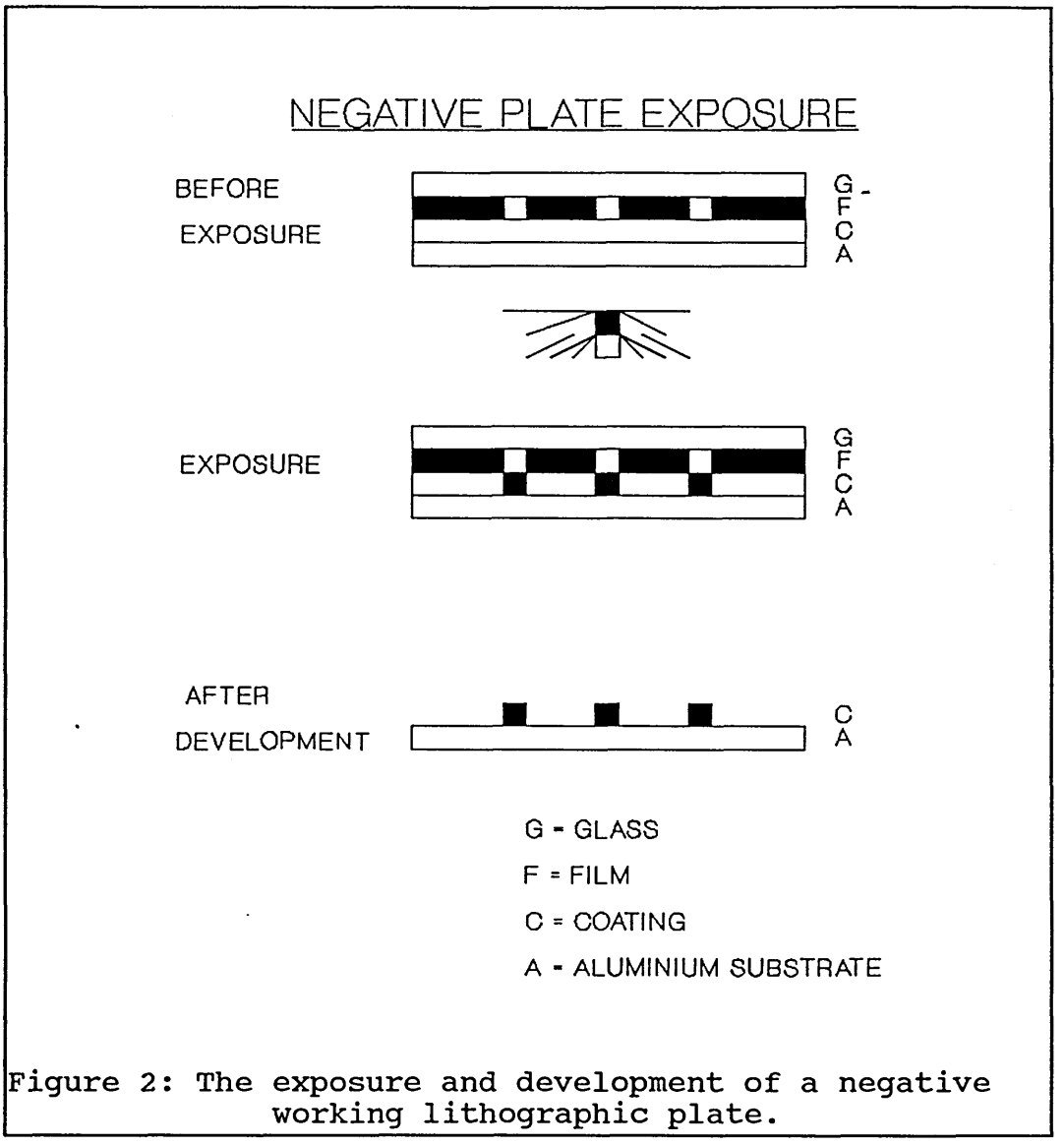


Figure 2: The exposure and development of a negative working lithographic plate.

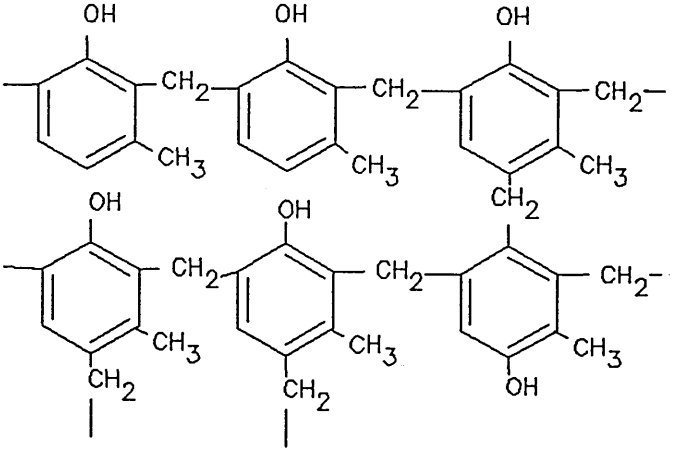
to the required final copy. Negative plates however contain chemically and physically resistant printing areas consisting as they do of crosslinked hardened resins. For long print runs where several hundred thousand copies are to be taken from a single printing plate, negative working plates are the natural choice. For shorter print runs of less than a hundred thousand copies, positives are often used though other considerations such as the toxicity of developers, colour change on exposure and cost will all influence the decision of the printer.

In order to demonstrate the importance of diazo compounds in the operation of lithographic printing

plates, the chemical processes involved will be explained in greater detail.

1.6 POSITIVE PLATE CHEMISTRY

The use of quinonediazides that form indene carboxylic acids on exposure has already been mentioned above. These are usually in simple mixture with an alkali soluble resin such as a cresol formaldehyde condensate (also called a cresol novolak (6)) .

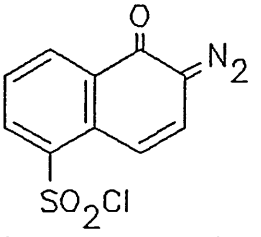


(6: Cresol novolak)

These resins are prepared by condensing a mixture of cresols (mainly the meta isomer) with formaldehyde in the presence of a small amount of catalyst (such as 2% oxalic acid). The water and some of the remaining cresols are removed by steam distillation.

Alternatively, rather than a mixture of novolak and quinone diazide, esters of the novolak can be used. Esters are usually at a low level such as 10 to 15% of available hydroxide groups and are prepared from quinone diazide sulphonic acid chlorides (7). The acid chloride functionality readily reacts with the phenolic hydroxy group.

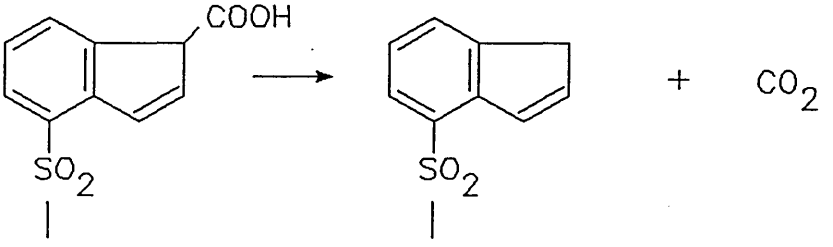
In both cases the quinonediazide or mixture of quinonediazides is present at such a level as to prevent development with aqueous alkaline developer solution. The formulation of the positive plate coating and the



(7: Quinonediazide sulphonic acid chloride)

developer are therefore interdependent. Typically the diazo compounds will comprise between 5 and 40% by weight of the coating solids.

Modern printing requires more than a coating that will provide selective development after exposure; the printer must be able to tell what areas have been exposed prior to development. This necessitates the use of a dye system that will undergo a colour change on exposure alone. Various acid/base dye systems have been used. The carboxylic acid formed from the quinone diazide readily decarboxylates (Scheme 4) and is unsuitable for providing a long lasting colour change in an acid/base dye system.

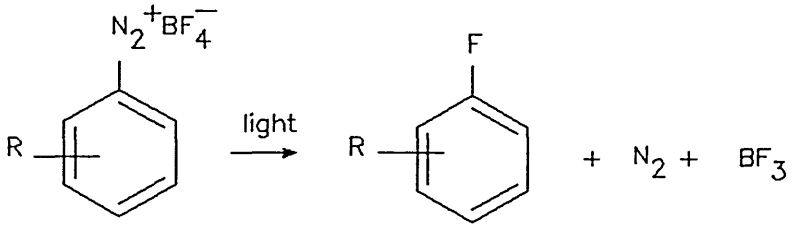


(Scheme 4: Decarboxylation of indene carboxylic acid)

A more satisfactory alternative has been to use a further group of diazo compounds that will release an acid on exposure. An example of this type is a diazonium salt with a BF_4^- or PF_6^- counterion. On exposure the diazonium salt decomposes and in part liberates nitrogen and the corresponding Lewis acid (Scheme 5).

This is the Balz-Schiemann reaction[11] which utilises the thermal decomposition of diazonium salts of this type to prepare fluoro derivatives.

The Lewis acid can accept a lone pair of electrons from the matrix liberating a proton that interacts with a



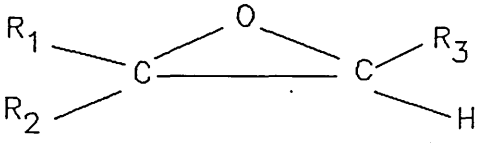
(Scheme 5: Photolytic decomposition of diazonium salt)

suitable dye to provide a colour change. This is explained in greater detail in section 1.8 .

1.7 NEGATIVE PLATE CHEMISTRY

Negative working plates utilise a chemical system that becomes less soluble in developer after exposure. As for positive working systems there is again a link between the composition of the developer and that of the photosensitive coating. In positive coatings mention was made of the liberation of Lewis acids when certain diazonium salts were exposed to light. The same diazonium salts have also been used in negative working systems with the Lewis acid acting as a cationic initiator for the polymerisation of epoxides. Epoxides are a class of monomers that may be polymerised via an anionic or cationic mechanism, but are relatively unresponsive to free radical initiation[12].

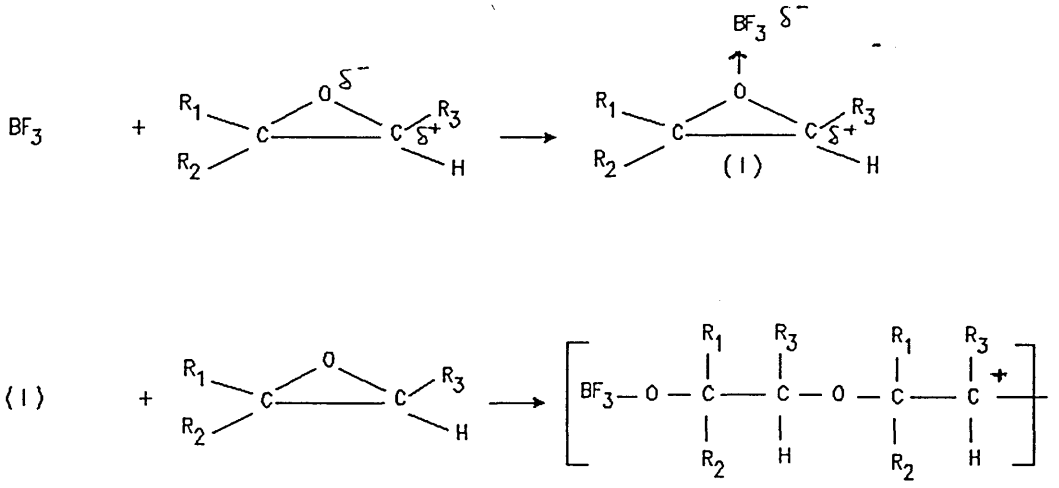
The epoxy resins used have the following general structure (8), below.



(8: Generalised epoxy resin structure)

Lewis acids are efficient initiators of the polymerisation of epoxides via a cationic mechanism. This type of initiator functions by accepting an electron pair from the epoxide ring (oxirane) oxygen atom as it forms a

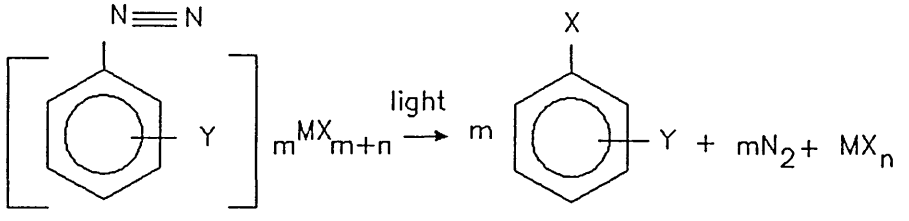
coordinate bond, resulting in ring opening, and a cationic polymerisation chain (Scheme 6).



(Scheme 6: Cationic polymerisation of epoxides)

Aryldiazonium salts with complex halide anions provide a convenient light sensitive source of Lewis acids. Aryldiazonium salts with the complex anions PF_6^-, BF_4^-, AsF_6^-, SbF_6^- etc. can be used giving rise to the corresponding Lewis acids: PF_5, BF_3, AsF_5, SbF_5.

The general principal of Lewis acid formation may be summarised as below in which $(MX_{n+m})^{m-}$ is a complex halide anion with a central element M, and m is the charge on the anion, as well as the number of halide ions complexed with the Lewis acid MX_n, and Y represents one or more substituents on the aromatic ring (Scheme 7).



(Scheme 7: Formation of Lewis acids during photolysis of diazonium salts)

One potential drawback of this system is that once the diazonium salt has been photolysed and the Lewis acid released, cationic polymerisation can proceed even in the dark, as with any Lewis acid initiated polymerisation.

Eventually, termination will occur due to consumption of all the available epoxide or by reaction with water. The presence of an observable "dark reaction", evidenced by increased developer resistance, is probably due to the coating acting as an oxygen barrier.

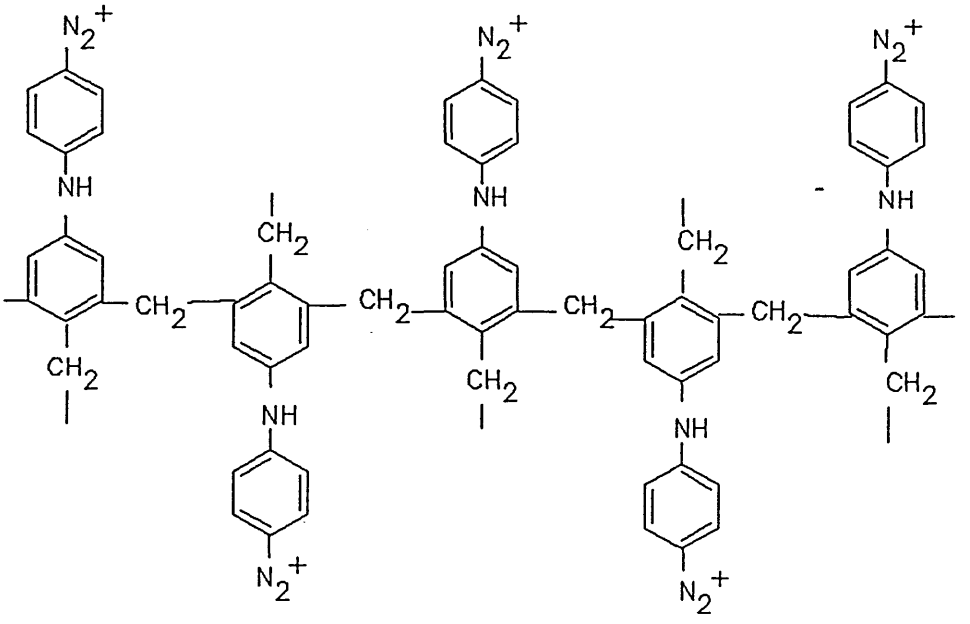
Consistent plate development can be obtained by a post-exposure heat treatment at about 80 °C for a few minutes. This gives plate development equivalent to that of a plate exposed to the same extent but after 30 minutes dark reaction.

The other problem with the cationic polymerisation system is that it requires a solvent-based developer. Chemically this is not a drawback, as there are plenty of solvents that will do the job. However the use of solvents is increasingly unacceptable to printers given that alternative negative plate systems have been devised that use aqueous based developers. Many of these also utilise diazo compounds but this time they are polymeric versions similar to those already discussed in Section 1.6 where they acted as acid release agents.

Diazodiphenylamine for example can be condensed with formaldehyde to give a polymer of the general structure (9).

This will often be used with an organic acid counterion such as toluene sulphonate to make the polymer sufficiently solvent soluble to be coated from quick drying solvents. The polymer is of low molecular weight and ionic . In its unexposed state it can therefore be developed with aqueous based developers. On exposure, nitrogen is liberated and the polymer crosslinks to give a higher molecular weight matrix that has lost its ionic character. This cannot be dissolved by aqueous developers.

These polymer systems are allied to the monomeric diazo salts used to provide a Lewis acid for positive plate colour change dyes (Scheme 5) and to the cationic polymerisation initiators described above (Scheme 7). As such they are subject to the same problems regarding their thermal stability; indeed the problem is worse from the



(9: Diazodiphenylamine/formaldehyde condensation polymer)

printer's point of view as a positive plate will still function without a colour change but a crosslinked unexposed negative plate is useless.

Diazodiphenylamine is one of a general class of aromatic compounds that contain the diazonium salt group attached to the aromatic nucleus. These compounds have been of interest for many years due to their high reactivity. Before commencing on a program of work related to the decomposition of diazodiphenylamine in lithographic systems it is first essential to review relevant work carried out on this and similar compounds.

1.8 REVIEW OF DIAZONIUM SALT DECOMPOSITION REACTIONS

1.8.1 The Balz-Schiemann Reaction

The Balz-Schiemann reaction, (often abbreviated as the Schiemann reaction) is a classical means of introducing a fluorine atom into an aromatic nucleus[13]. It is the most widely studied decomposition reaction of diazonium salts and thus forms a useful introduction to their chemistry. It is usually carried out by the

pyrolytic decomposition of an aromatic diazonium fluoroborate yielding an aryl fluoride. This provides a useful method of converting aromatic amines into fluorides (Scheme 8).

$$ArNH_2 \xrightarrow{NaNO_2/HCl} ArN_2^+Cl^- \xrightarrow{NaBF_4} ArN_2^+BF_4^-$$

$$ArN_2^+BF_4^- \xrightarrow{heat} ArF + BF_3 + N_2$$

(Scheme 8: Conversion of aromatic amines to the fluoride via the Balz-Schiemann reaction)

Addition of fluoroboric acid or fluoroborate to the diazonium salt solution precipitates the sparingly soluble diazonium fluoroborate. The dry salt is gently heated to the decomposition point yielding the aryl fluoride. The method depends on the remarkable stability (relative to other diazo compounds) of the dry diazonium fluoroborates. These do not explode when heated but undergo smooth decomposition. The reaction is of wide application and overall yields of 70% are often obtained [14].

Three possible mechanisms have been suggested (scheme 9) although the mechanism of decomposition of diazonium fluoroborates is not definitely known [11].

(a) Free radical

Slow $\quad ArN_2^+BF_4^- \rightarrow Ar^\cdot + F^\cdot + BF_3 + N_2$

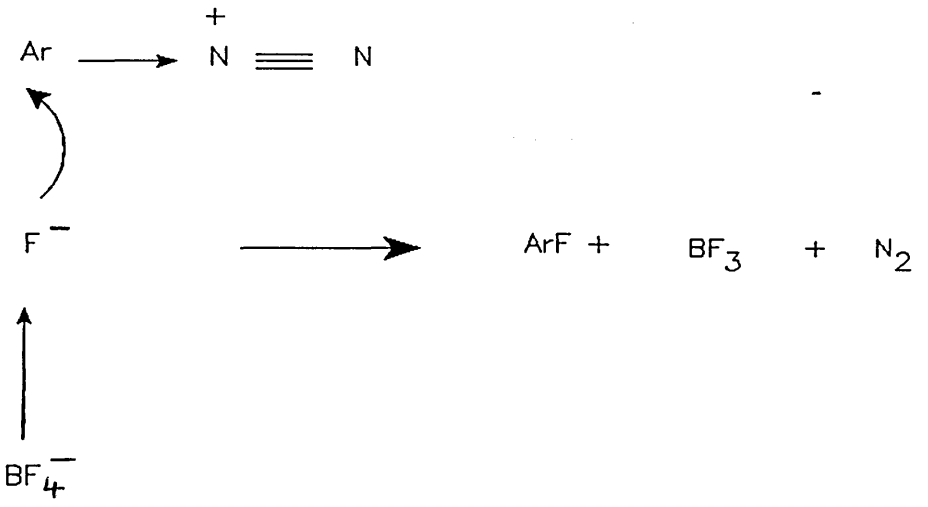
Fast $\quad Ar^\cdot + F^\cdot \rightarrow ArF$

(b) Ionic, involving a carbonium ion

$$ArN_2^+BF_4^- \rightarrow Ar^+ + BF_4^- + N_2$$

$$Ar^+ + BF_4^- \rightarrow ArF + BF_3$$

(c) Rearrangement



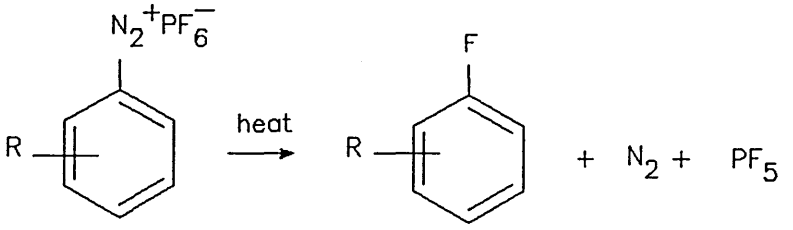
(Scheme 9: Postulated reaction mechanisms for the Balz-Schiemann)

By far the most likely is scheme 9b. Evidence for this scheme involving a phenyl cation intermediate comes from analysing the products formed by carrying out the Schiemann reaction in the presence of substituted aryl systems[15]. The products formed are in accordance with electrophilic substitution; meta directing groups for electrophilic substitution give rise to meta-arylation. Radical attack or rearrangement would lack specificity and not give the observed products.

The attacking species after the formation of the cation intermediate has been shown to be BF_4^- or F^-[16], depending on the circumstances of the reaction. Adding an excess of BF_3 did not affect the decomposition product distribution. This indicates that any mechanism involving dissociation of BF_4^- into F^- and BF_3 is unlikely. Excess bromine was added to the reaction mixture as a free radical trap in one experiment. Since no ArBr formed, radical reactions are also improbable.It is not unreasonable that an intermediate as reactive as Ar^+ should be capable of attacking BF_4^- without waiting for it to dissociate into F^- ion.

Other anions such as SbF_6^-, AsF_6^- and especially PF_6^- have been used successfully, in many cases with better yields[17]. The success of the Schiemann reaction via the fluoroborate method depends on the isolation of the intermediate diazonium fluoroborate and the quantitative conversion of the dry salt to the aromatic fluoride without interference by side reactions. The scope of the method is limited by the relatively high solubility of the fluoroborates in parent amino-aromatic acids and aminophenols, thereby making isolation of the salts difficult. The yield is restricted to 65-70% as a result of side reactions caused by a combination of impurities and the presence of the powerful Lewis acid, boron trifluoride, in the hot reaction mixture. Hexafluorophosphate intermediates are less soluble than the corresponding fluoroborates. This permits a more thorough washing to eliminate impurities without significantly affecting yields.

The reaction in this case yields phosphorus pentafluoride (scheme 10) which is not as strong a Lewis acid as is boron trifluoride and side reactions are minimised.

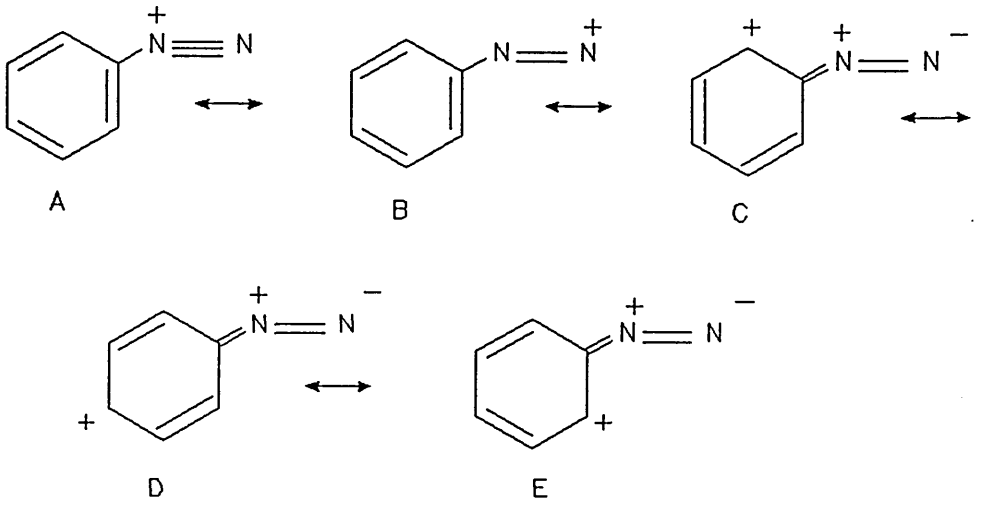


(Scheme 10: Use of hexafluorophosphate in the Balz-Schiemann reaction)

More recent developments include the addition of solvents or salts to moderate the decomposition[18] and the use of ultrasound[19] to provide an alternative energy source.

1.8.2 Diazonium salt structure

Diazonium salt structure must be understood if the reactions that they undergo are to be adequately explained. Dewar[20] has expressed the view that the arenediazonium ion owes its existence and properties to the fact that in its canonical forms the two nitrogen atoms are attached to the arene nucleus by a single covalent bond (functions A and B in scheme 11 below). Being deficient of one electron, they carry a unit of positive charge, which can be balanced only by a strong anion, either external or internal (the π-electrons of the benzenoid aromatic system being quite unable to provide the charge required). In consequence of further and more extensive electronic shifts, the arene nucleus has a small quinoid function (functions C- E). Five of the functions comprising the resonance hybrid are shown in scheme 11.



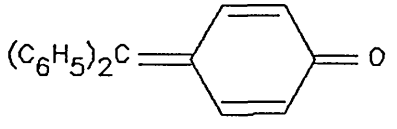
(Scheme 11: Canonical forms of the diazonium salt)

An X-ray study of benzenediazonium chloride carried out by Romming[21] confirmed the correctness of the classical linear arrangement of the C-N-N chain. The benzenediazonium ion was found to be planar, with the N≡N bond length equal to that in gaseous nitrogen. The chloride ions were found to be arranged in a plane that bisects the N-N bonds, and the distance of each nitrogen atom from the chloride ions is nearly the same. This

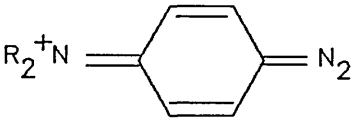
evidence suggests that the positive charge is shared about equally between the nitrogen atoms, as in functions A and B, but a later study of near-ultraviolet absorption, fluorescence emission and excitation spectra of benzenediazonium tetrafluoroborate in conjunction with molecular orbital calculations[22], led to the conclusion that the N_1 atom bears almost all of the positive charge. In further X-ray studies[55], data were obtained for the crystal structure of p-diazo benzene sulphonate. It was calculated that the charge on the nitrogen atoms was +0.31 for N_1 and +0.12 for N_2.

The function A is commonly used to denote the ground state of the benzenediazonium cation and arenediazonium cations in general. The function B, having a terminal electron sextet, denotes the diazo-form parent of covalent diazo compounds. Functions C, D, and E are quinoid states concerned in activation in bimolecular nucleophilic substitution of the arene nucleus. For aromatic or heterocyclic nuclei other than the benzene ring there may be the same, or more or fewer canonical structures of the resonance hybrid with corresponding change in reactivity.

Function D makes a large contribution to the hybrid of the N-substituted p-aminobenzenediazonium ion. In one study[24], a comparison of the U.V.-visible absorption spectra of various p-aminoaryldiazonium salts with that of diphenylquinomethane (10), indicated that these diazonium compounds also have a quinoid structure (11).



(10)



(11)

(10,11: Quinoid structures of diphenylquinomethane and the p-amino aryl diazonium ion)

It was observed that p-aminoaryldiazonium salts are a group of exceedingly stable compounds when compared with simple aromatic diazonium salts. They are usually yellow or orange in colour while the great majority of other

diazonium compounds are colourless. It was inferred that the quinoid structure conferred increased thermal stability on these diazonium compounds.

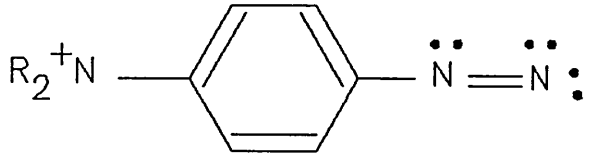
The infra-red spectra of diazonium salts show a characteristic absorption band between 2100 and 2300 cm^{-1} which has been attributed to the N-N stretching frequency[25]. Some workers[26] have concluded that, for a given cation the position of this band is independent of most anions. However, since the infra-red spectra of fluoroborates showed peaks at slightly higher frequencies than the spectra of other salts, it was concluded that the fluoroborates were ionic but that there was some covalent bonding between the cation and anion in the other salts[27]. The covalent bonding is due to direct interaction between the lone pairs of the halide ions and the vacant orbital of the diazonium group. This interaction does not occur with the salts of the very strong complex fluoro acids.

The division of diazonium salts into two types based on their reactivity and U.V. absorption characteristics mentioned above, is also apparent in the N-N stretching frequencies of the crystalline solids. A high N-N frequency is associated with decomposition by a heterolytic mechanism, whilst partial covalent character in the solid state is associated with homolytic decomposition.

Attempts have been made to correlate the N-N stretching frequency with the electronic effects of other substituents - as measured by the Hammett function[26]. Observations which were made on the solids showed trends in the right direction but these trends do not hold as well as for other groups such as C=O and N-H. Such observations should ideally be made on solutions and a complicating factor with cations such as the diazonium ions is that solvation is much greater than for uncharged molecules. Since the electronic effects of solvation may well be in an opposite direction to those of the substituent groups, an overall complexity is not unexpected. More recent interpretations of decomposition

data in terms of Hammett and related functions are described in further detail later (Section 1.8.3).

The infra-red spectra of diazonium salts of p-dialkylaminoanilines show a number of features which are different from other diazonium salts. Two infra-red bands are observed in the N-N stretching region in both the solid and the solution[27]. Another intense band near 1100 cm^{-1} is also observed. These differences correspond with those observed differences in ultra-violet/visible spectra and reactivity already alluded to above. These results indicate that in addition to the quinoid form as in scheme 11 structure D, the structure (12), in which charge transfer from the diazonium group to the amino group has taken place, is of major importance in these cations.



(12: Charge transfer from the diazonium group to the amino)

The intense infra-red band at 1100 cm^{-1} is assigned to C-N vibrations involving the dialkylamino group; the charge would be expected to increase the intensity of the absorption. These amino substituted diazonium salts have low N-N stretching frequencies, even for the fluoroborate salt. There is less variation in the N-N frequency for these salts. This indicates that due to charge transfer from the diazonium ion to the amino substituent, there is less interaction between the N-N group and the complex anion.

The reduced interaction will be investigated as a means of improving the stability of the diazonium group.

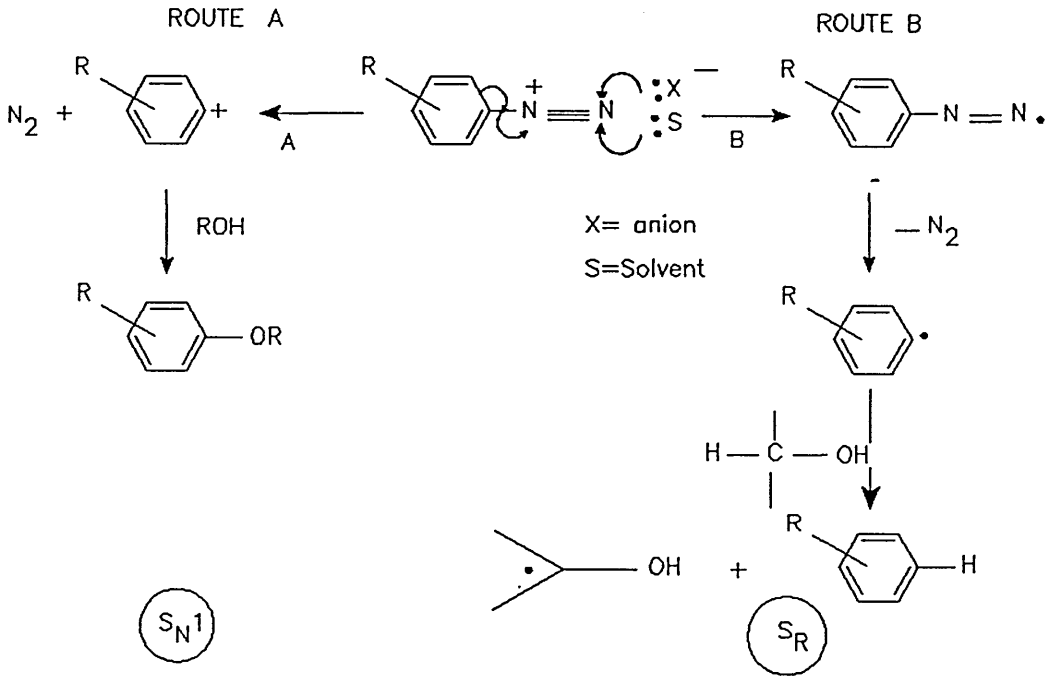
1.8.3 Decomposition Investigations

As will be described in this introduction to decomposition mechanisms, a variety of mechanistic pathways have been postulated. This is at first surprising since only an S_N1 type dissociation of the diazonium ion to an aryl cation and nitrogen would be expected by analogy with the decomposition of aliphatic diazonium ions and from the extremely high stability of the nitrogen molecule.

The systematic nomenclature of substitution reactions proposed by Bunnett[28] and promoted by Zollinger[29] (one of the most active workers in this field) is that regardless of mechanism, all reactions in which both nitrogen atoms of an azo or diazo compound are replaced by another group are designated dediazoniations. This term is preceded by the name of the entering group. A Gomberg-Bachmann arylation is accordingly designated as aryl-dediazoniation, a hydrolysis as hydroxy-dediazoniation and replacement of the diazo group by hydrogen as hydro-dediazoniation. Although the term cannot be regarded as a graceful addition to the chemical terminology it has been found convenient and it is therefore used in the present account.

On heating, aromatic diazonium salts may eliminate nitrogen by two fundamentally different mechanistic pathways, heterolysis and homolysis[29]. In heterolysis the C-N bond is broken leaving an aryl cation and nitrogen, while in homolysis aryl radicals and nitrogen are produced. The reaction mechanisms of the thermolysis and photolysis of aryl diazonium salts are still not known with certainty in spite of the fact that the problem has now been examined for over a century[30].

The discussion centres on whether radical (homolytic) or ionic (heterolytic) mechanisms predominate under a particular set of circumstances. The differences between the two mechanisms can be seen in scheme 12.



(Scheme 12: Cationic(A) and radical(B) mechanisms for diazonium decomposition.)

On the assumption that in the C-N bond in the diazonium salt one of the two bonding electrons belongs formally to each of the two partners, a further electron must be supplied either from the aryl residue (route A) or from the anion or solvent (route B) for the separation of molecular nitrogen. In route A, an "internal" electron transmission process, an aryl cation is produced which reacts with a nucleophile present in the local environment eg. water or an alcohol, to form the substitution product (phenol or phenylalkyl ether) and a (low-energy) proton. This corresponds to the conventional S_N1 process.

In route B, an "external" electron transfer process, an aryl radical is produced which is converted to the corresponding aromatic hydrocarbon (reduction product) by hydrogen abstraction from a C-H bond of another substance or the solvent. The radical produced from the H-abstraction is generally very reactive and frequently able to transfer in turn one electron to the aryl diazonium salt, so that the result is a chain reaction leading to polymeric products (Scheme 13).

$$Ar^{\cdot} + R\text{-}H \rightarrow Ar\text{-}H + R^{\cdot}$$

$$ArN_2^{+} + R^{\cdot} \rightarrow Ar^{\cdot} + R^{+} + N_2$$

$$Ar^{\cdot} + ArN_2^{+} \rightarrow Ar\text{-}Ar^{+} + N_2$$

$$Ar\text{-}Ar^{+} + R^{\cdot} \rightarrow Ar\text{-}Ar^{\cdot} + R^{+}$$

$$Ar\text{-}Ar^{\cdot} + ArN_2^{+} \rightarrow Ar\text{-}Ar\text{-}Ar^{+} + N_2 \quad \text{etc.}$$

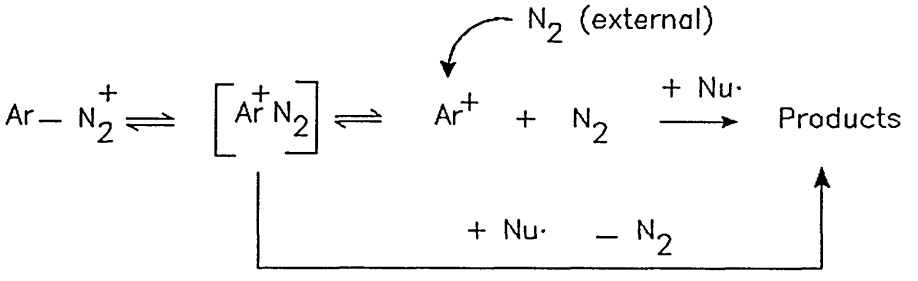
(Scheme 13: Formation of polymeric products from radical dediazoniation)

On the basis of classical studies by Crossley et al[31], it was long accepted that the hydrolysis of arenediazonium salts in acid solution proceeded by an S_N1 mechanism (Scheme 12A). Doubt was cast on this concept when reactions were discovered whose kinetics were influenced by the concentration of nucleophiles present in the system[32].

An investigation of the effects of substituents on the kinetics of dediazoniation in water[33] in terms of dual parameter substituent constants was compatible with the intermediacy of an aryl cation but not with an S_N2-type transition state. The occasional influence of nucleophile concentration on the reaction rate could not be interpreted in this way. It could however be explained by the possibility that the formation of aryl cation and molecular nitrogen is reversible.

This surprising reaction is demonstrated by N^{15} labelling experiments under high nitrogen pressures[34,35]. The dediazoniation rate, the isotopic N-N rearrangement, and the exchange reaction of the diazonium group with external nitrogen in β-N^{15} labelled diazonium salts were measured under a constant pressure of 300 atmospheres of

nitrogen. The results are interpreted in terms of a "molecular-ion" pair and a phenyl cation intermediate. The reverse step of the formation of the phenyl cation and nitrogen is the first evidence for a reaction of nitrogen molecules with a purely organic reagent in solution. The relatively small influence of substituents on the amount of isotopic rearrangement and exchange with external nitrogen indicates that these reactions are mechanistically of the same type as solvolysis, namely additions of the nitrogen nucleophile to the phenyl cation. This is summarised below (Scheme 14). The first intermediate is a tight nitrogen aryl cation molecule-ion pair, and it is responsible for the observed rearrangement reaction. The exchange reaction occurs at the second intermediate which is the free (no nitrogen) aryl cation. Dediazoniation products can be formed by nucleophilic attack on both intermediates.



(Scheme 14: Reversible dediazoniation via a molecular-ion pair intermediate.)

Hence the aryl cation is a steady-state intermediate which must lead to a drop in the overall reaction rate on increasing the concentration of nitrogen and to a rise in the rate on increasing the concentration of nucleophiles.

The behaviour of diazonium salts dissolved in methanol has been studied in detail and is of particular interest because of the influence of the atmosphere (containing or devoid of oxygen)[36]. Methoxy-dediazoniation usually predominates in the presence of oxygen, whereas hydro-dediazoniation generally predominates under nitrogen or argon. The experiments performed with rigorous

exclusion of oxygen are compatible with a radical chain mechanism (Scheme 15).

$$Ar^{\cdot} + CH_3OH \rightarrow Ar\text{-}H + {}^{\cdot}CH_2OH$$

$${}^{\cdot}CH_2OH + Ar\text{-}N_2^{+} \rightarrow Ar\text{-}N{=}N^{\cdot} + CH_2O^{+}H$$

$$Ar\text{-}N{=}N^{\cdot} \rightarrow Ar^{\cdot} + N_2$$

(Scheme 15: Radical mechanism for hydro-dediazoniation in methanol in the absence of oxygen)

This chain reaction is reasonable since it would give $CH_2O^{+}H$ from which two thermodynamically highly stable compounds, formaldehyde and methoxymethanol, are formed (Scheme 16).

$$CH_2O^{+}H + CH_3OH \rightarrow CH_2O + CH_3O^{+}H_2$$

$$CH_2O + CH_3OH \rightarrow CH_3OCH_2OH$$

(Scheme 16: Formation of stable entities from radical dediazoniation)

A series of product analyses for experiments in the presence of radical scavengers such as 2-methyl-2-nitrosopropane and iodobenzene clearly demonstrate the intermediacy of aryl radicals. The homolytic dediazoniation generally predominates with diazonium ions rendered more electrophilic by suitable substitution at the aryl group.

The most widely used classification of substituent effects on rate and equilibrium constants was that developed by Hammett. Substituents that stabilised the formation of positive charges and destabilised the development of negative charges at the reaction centre were known as electron-donating substituents, and the

substituents of the opposite type were known as electron-withdrawing substituents. Regularities in substituent effects were observed under many different conditions, most commonly with aromatic compounds, particularly meta- and para-substituted ones. The lack of a corresponding regularity for ortho substituents indicated that the steric interactions between substituent and reaction centre masked electronic factors.

The original data used the ionisation constants for a range of substituted phenylacetic and benzoic acids which were readily available for a large number of substituents. Thus if K is the equilibrium constant for the substituted benzoic acid and K_o is the equilibrium constant for benzoic acid, a parameter σ (the substituent constant) is defined by the following equation:

$$\sigma = \log K - \log K_o = -pK_a + (pk_a)_\sigma$$

Since pk_a values are affected by both solvent and temperature, σ is arbitrarily defined as referring to aqueous solution at 25 °C. Electron withdrawing groups, such as NO_2, increase the ionisation constant K of benzoic acids because they stabilise the carboxylate anion. The pk_a is numerically smaller than that of benzoic acid, and σ is consequently positive. Electron-donating groups, CH_3 for example, decrease the equilibrium constant, and so their σ values are negative[38].

Apart from the deviation from the Hammett equation due to steric effects, there are some other large systematic deviations that came to Hammett's attention[39]. These were in reactions in which there was at the reaction centre (in the reactants, the products or both) a group capable of strong resonance electron donation to the ring. Deviations were not observed with meta-substituted compounds, but with para-substituted compounds in which the para substituent was a group like nitro, cyano, or acetyl capable of withdrawing electrons strongly by a resonance effect. The deviations were all in such a direction as to indicate that the presence of a strongly resonance electron withdrawing group and a strongly

electron-donating group para to each other on an aromatic ring led to species that were more stable than would be expected from the simple Hammett equation. This form of resonance stabilisation is apparent from the various canonical forms given for the diazonium group in scheme 11 and particularly when para substituted with electron donating groups as in structures (10) and (11).

To cover cases of the type just described, Hammett assigned to various strongly electron-withdrawing para substituents like nitro and diazo, special substituent constants for use in reactions in which there is a group capable of strong electron donation at the reaction centre. Such substituents later became known as sigma minus (σ^-) values.

The following table shows the value assigned to the diazo group and others for comparison.

Table 1: Values of σ^- for para substituents calculated from substituted phenol acidity values.

Substituent	σ^-	Substituent	σ^-
N_2^+	3.2*	CHO	0.98
NO_2	1.23	CO_2H	0.73
SOMe	0.17	CO_2Me	0.74
SO_2Me	1.05	CO_2Et	0.74
SO_2CF_3	1.36	$CONH_2$	0.62
SO_2NH_2	0.94	CN	0.99
SMe_2^+	1.16*	CF_3	0.56

* Substituent constants for electrically charged species are relatively unreliable[40].

Since the initial proposal of the Hammett equation, many phenomena have been found that do not correlate well with the original constants of Hammett. The resulting proliferation of alternative sets of σ values for special systems or applications has now "reached the point of absurdity"[32].

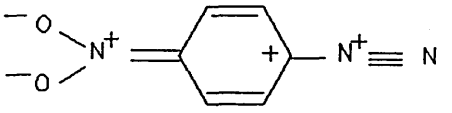
The original discrepancy appeared to be due to the increased importance of resonance effects relative to non-resonance effects, giving rise to the σ^+ and σ^- sets of substituents. If both pure field and inductive non-resonance effects are lumped together under the name field effects, there are found to be not just two or three levels for the relative importance of field vs. resonance effects but a broad continuum for equilibria, rates, and other properties of interest. This led gradually to the proposal of numerous additional σ scales, each based experimentally on a different single reaction series or occasionally on a pair or larger number of reaction series, and each representing a different blend of field and resonance effects, with the proportion uncertain. Swain et al[33] have shown that it is possible to reduce more than 20 sets of substitution scales to an expression derived from $\sigma = fF + rR$ where σ is any substituent constant, F and R are field and resonance constants and f and r are weighting factors.

The dediazoniation rates of meta- and para-substituted benzene diazonium chloride salts in water was studied extensively by Swain et al[41]. Excellent correlation coefficients of 0.984 for ten meta substituents and 0.992 for seven para substituents, including hydrogen were obtained between observed and calculated values for relative reaction constants. On the other hand the same data for para substituents gave entirely random Hammett plots with a correlation coefficient "so poor as to be quite imaginary".

However, the effects of substituents on the rate of the homolytic reaction could not be correlated with any substituent constants (such as Hammett, Taft, Swain etc.)[37]. This is often the case for reactions that proceed via a radical mechanism.

Hammett and related functions are therefore of limited value for elucidating the influence of particular substituents. Their use is further complicated by other factors. For example, with weakly electrophilic

arenediazonium ions, the heterolytic mechanism predominates even in the absence of oxygen; with chlorinated or brominated arenediazonium salts this occurs only in the presence of oxygen. Thus oxygen rapidly terminates the radical chain in these cases. Radical decomposition nevertheless prevails under oxygen with the p-nitrobenzenediazonium ion. This has been attributed[42] to an increased contribution from the resonance form (13).



(13: Resonance form of the p-nitrobenzenediazonium ion)

The mechanism of diazo decomposition is influenced not only by substituents in the arene ring but also by the nature of the solvent, certain additives and other factors.

Studies of the products of reactions of benzenediazonium tetrafluoroborate in 2,2,2-trifluoroethanol (TFE)[43] show that the reaction is entirely heterolytic. Benzene, a typical product of homolytic reactions, is not formed.

In mixtures of TFE with other solvents such as benzene, toluene, anisole, and nitrobenzene, the yield of the appropriate biphenyl increases with the nucleophilicity of the aromatic substrate.

An interesting demonstration of the complex behaviour of diazo decompositions caused by the presence of competing mechanisms was a study undertaken by Zollinger and co-workers[44]. By adding increasing amounts of pyridine to a solution of benzenediazonium tetrafluoroborate in TFE, the decomposition mechanism was gradually changed from heterolytic to homolytic. Five products were isolated: (a) phenyl 2,2,2-trifluoroethyl ether, (b) fluorobenzene, (c) benzene, (d) biphenyl and (e) phenylpyridines. In addition a diazo tar was formed

increasingly as the pyridine level was increased. Of these products, (a) and (b) result from heterolytic mechanisms, but (c), (d), (e) and probably the diazo tar are formed by homolytic mechanisms. In the absence of pyridine, (a) and (b) were the sole products, but as the amount of pyridine was increased the yield of these substances fell sharply, whereas that of (c), (d), (e) and the tar rose. The formation of tar was noticeably promoted by the presence of oxygen. This latter point is surprising as oxygen is regarded as a radical inhibitor, whereas the formation of a diazo tar is usually indicative of a radical reaction mechanism.

Even so small a content of oxygen as 60-100 ppb in a nitrogen atmosphere has been found to result in a marked increase in the rate of dediazoniation of p-chlorobenzenediazonium tetrafluoroborate in aqueous solution at pH 9 and 20 °C. A half-life time of more than 80 hours with less than 5 ppb of oxygen fell to 30 hours in the presence of 60-100 ppb oxygen. When the reaction was conducted in a vessel of Teflon which absorbs oxygen upon its surface, a further marked increase in reaction rate was observed[45].

Dediazoniations in a series of solvents exhibit a surprising and apparently inexplicable variety of mechanisms. There is not only one heterolytic and one homolytic decomposition pathway but several. Presumably further mechanisms may apply in other less studied systems[29].

In semiquantitative terms the concept of dual solvent parameters developed by Gutmann[46] can be applied to dediazoniations. Solvents can behave as donors or acceptors in the interactions with solutes. These two parameters were determined independently with the aid of two suitable standard substrates. Two parameters, the donor and acceptor numbers, were introduced. Depending on the kind of solvation, one of the parameters can outweigh the other.

A similar approach was adopted earlier by Koppel and Pal'm[23] who sought to quantify the effect of the solvent by introducing four parameters which describe the nonspecific and the specific solvation as the result of the electrophilic and the nucleophilic properties of the medium.

In a survey of solvent systems[29] it was found that the tendency towards radical reactions follows the series of Gutmann donor numbers and Koppel and Pal'm nucleophilic solvent donor values where they are known.

It might be expected that the lone pair of the β-nitrogen acts as a donor to solvents having better acceptor properties, thus favouring heterolysis. However since the rate of heterolytic dediazoniation is reported[41] to remain roughly constant in numerous solvents, heterolysis seems much less susceptible to acceptor effects than homolysis does to donor effects.

This evidence only suggests that a specific nucleophilic solvation is necessary for homolytic dediazoniation. No information is forthcoming about the kind of interaction between the solvent molecule and the diazonium ion (whether it is covalent bonding, donor-acceptor complex, etc.).

Although solvation is essential for the actual electron transfer to the diazonium ion, it is not the only condition. The donor must also have a favourable redox potential, i.e. it must be capable of forming a relatively stable species on release of an electron.

Some interesting work by Becker et al [30] has demonstrated that of two fundamentally possible dediazoniation reactions (as shown in scheme 12), the reaction is favoured in which the electron required for elimination of nitrogen can be supplied with the lowest expenditure of energy. For heterolytic reactions this will be intramolecular electron transfer from the aryl group to form an aryl cation with or without participation of an external acceptor solvent. In homolytic dediazoniation, it is electron transfer from an external donor. From

correlation tables between the oxidation potential of the donor and reduction potential of the diazonium ion, they calculated what combinations of diazonium salt and solvent or additives would react ionically or radically for preference during thermal or photochemical decomposition of diazonium salts. They concluded that "the thermal and photochemical decomposition reactions of the aryl diazonium salts thus acquire a consistent theoretical basis".

In conclusion, though it should be possible to quantitatively predict the reactivity of donor groups or solvent in the matrix from a dual-parameter equation, the complex nature of the kinetics of homolytic/heterolytic dediazoniations is likely to prevent the obtaining of comparable rate constants[29].

1.8.4 Stabilised diazo compounds

The earliest attempts at stabilising diazonium salts were instigated by problems due to froth formation caused by diazo decomposition during the printing of naphtholated cloth. Experiments as long ago as 1891 [47] utilised various metallic salts and obtained satisfactory results with zinc chloride, which forms double salts with many diazonium compounds. Later zinc chloride became one of the chief agents in the manufacture of stabilised diazo compounds.

The double salts have the general formula $(ArN_2Cl)_2,ZnCl_2$ and were easily prepared by addition of a slight excess of an aqueous solution of zinc chloride to the diazo solution. The term "diazonium double salt" is misleading in that it suggests an association between two salts, each ionised. In most cases the salts are derived from a diazonium cation and a complex anion. Thus the structure of the diazonium zinc double chlorides is more clearly represented as $(ArN_2^+)_2ZnCl_4^{--}$. Studies of the crystal structure of the tetrachlorozincate have shown that the zinc atom is surrounded by four halogen atoms, arranged nearly tetrahedrally. The results have confirmed

that there is no direct link between the nitrogen and the metal atom.

Although many of the metal complex anion salts are water soluble, they are generally insoluble in organic solvents. This has limited their use in lithographic printing where the high plate production speeds requires a quick drying organic solvent. Alternative complex salts with metal-free anions are more commonly used. By adding fluoroboric acid or its sodium salt to an aqueous solution of the diazonium chloride salt, a crystalline precipitate of the fluoroborate salt is produced. The potential of fluoroborate salts for stabilising diazonium salts was recognised soon after their discovery, in conjunction with that of hexafluorophosphate[49].

Another type of stabilisation by alteration in the anion was discovered by Becker[50] who found that addition of one equivalent of naphthalene-1-sulphonic acid for each diazo group of an aqueous solution of a diazonium mineral acid salt resulted in the precipitation of a crystalline precipitate that was thermally more stable than the original salt. Subsequently each pair of diazonium compounds and arenesulphonic acids was found to require separate study to find the best conditions of isolation[51].

In aqueous solution diazonium arenesulphonates are often more stable than the corresponding salts with mineral acids in similar conditions. A quantitative study of naphthalene sulphonates [52] concluded that any attempt to express the stabilising effect must include a reference to the pH and temperature concerned since a change in these factors can easily overwhelm the effect of even a high concentration of the stabiliser. The stabilising effect of five molecular proportions of naphthalene-1,5-disulphonate was only just apparent after 2 hours, when decomposition had reached 48%.

The final, and in many ways most interesting, development in attempts to stabilise diazonium salts is that of host-guest complexes. These occur when two or more molecules fit closely and are held together by

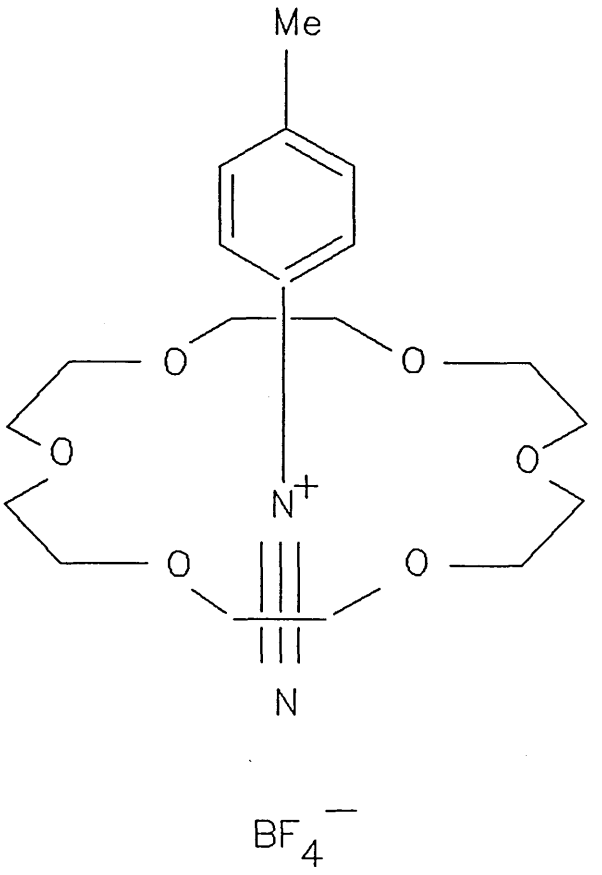
comparatively weak hydrogen bonds, ion pairing, π-acid to π-base interactions or van de Waals forces. In many examples an arenediazonium salt is the "guest" molecule and is associated with a cyclic polyether as the "host" by virtue of the fact that the diazonium group can be accommodated within the central cavity of the cyclic ether.

An account of such molecular complexes has been given by Cram et al[53], in which it is stated that "the host fits like a collar around the $^{+}N{\equiv}N$ neck of the guest". This analogy is appropriate although the "collar" is usually closed and completely encircles the "neck" (as shown in structure 14 below).

A study of molecular models of 18-crown-6 cyclic polyethers and of arenediazonium cations suggested to Gokel and Cram[54], that host-guest complexes might be formed between such compounds. Subsequent experiments showed a shift in ^{1}H NMR signal with the methylene singlet of the crown being shifted from 3.62 to 3.58 ppm. in the presence of p-toluenediazonium tetrafluoroborate. Increased solubility and the N.M.R. signal shift were interpreted as being caused by complexation with the oxygen atoms of the crown ether turned inward towards the positive charge upon the diazonium ion as shown in (14).

The average diameters of the crown ethers that showed evidence of complexation were estimated from the models as being 2.9 and 2.6 Å. The cavities can therefore accommodate the diazonium group, which has a cylindrical diameter estimated as 2.4 Å from the data of Romming[55]. Other similar crown ethers with slightly smaller cavities (2.2 Å) failed to form a complex with p-toluenediazonium tetrafluoroborate.

The thermal stability of this compound in 1,2-dichloroethane at 50 °C was found to be considerably increased by the presence of 18-crown-6 polyether, and the rate of decomposition was further retarded as the concentration was increased beyond 1 mol per mol of diazonium salt[56]. This was the first reported use of crown



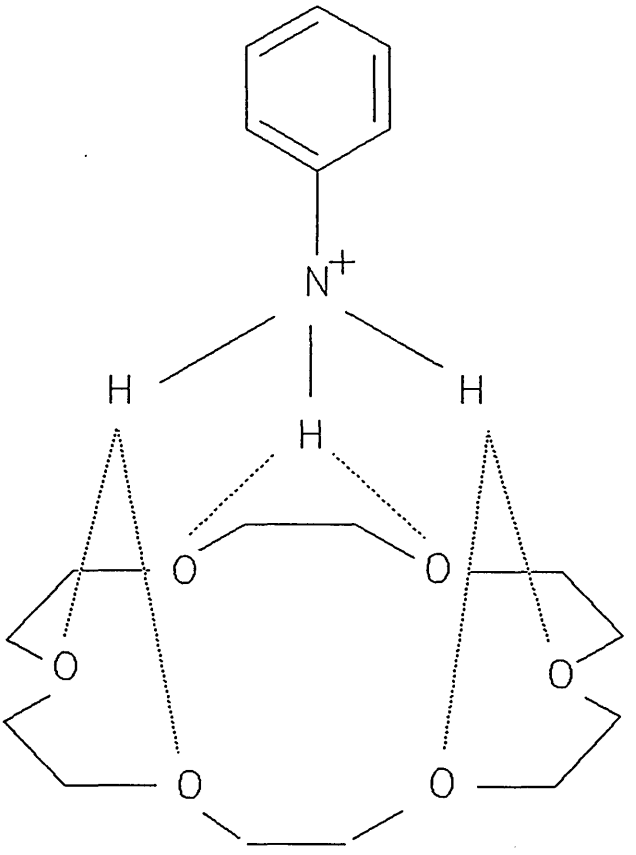
(14: Host-guest complexation of diazonium by 18-crown-6 cyclic ether)

ethers to stabilise diazonium salts although similar stabilisation by a "macrocyclic effect" had been reported for decompositions of metal ion complexes.

Later members of the same research group[57] found that 15-crown-5 polyether, having a cavity too small to accommodate the diazonium ion, gave high yields of fluorinated decomposition products and actually increased the rate of gas evolution.

A comparison of the complexes of arenediazonium compounds with those of anilinium cations (15) showed the former to be much more drastically affected by substitution ortho to the positive charge centre[58].

This is due to the anilinium ion positioned on top of the macrocycle rather than inserting itself into the ring cavity as does the diazonium ion. The addition of just one ortho methyl group to the benzenediazonium ion effectively eliminates complexation altogether, whereas the stability



(15: Reduced complexation of anilinium cation)

of the anilinium complex drops gradually with each addition of a methyl group adjacent to the ammonium group.

An extensive study[59] of complexation by macrocyclic multidentate compounds showed that of over 50 such compounds 21-crown-7 gave the strongest complexation. Although the cavity in such a compound appears to be rather too large for the diazonium ion, a degree of flexibility may be assumed to be present in rings of this size. It was found that complexation is promoted by electron-donating substituents in aromatic rings forming part of the macrocycle.

Electronic factors were found to have a considerable effect on the binding of 18-crown-6 ether to arenediazonium salts[60]. As para substituents in the benzenediazonium ion become increasingly electron donating the stability of complexes with 18-crown-6 progressively declines. Indeed complex stability is almost completely

lost when the para substituent is $N(CH_3)_2$ or $N(C_2H_5)_2$. This was presumed to be due to the delocalisation of positive charge away from the diazonium group (as discussed in section 1.8.2). Thus the compounds with the more effective positive charge on the nitrogen atoms of the diazonium ion form the stronger complexes. This has implications for the effectiveness of this kind of complexation for the stabilisation of diazodiphenylamine salts as used in lithographic systems, as they contain a substituted amino group para to the diazonium ion.

A particularly interesting study by Bartsch and Juri[61] has cast doubt on the original "host"-"guest" relationship in that similar stabilisation of diazonium ions has been observed by open, none-ring polyethylene glycol dimethyl ethers. These ethers have structures $Me(OCH_2CH_2)_nOMe$, and are commonly known as glymes. In diglyme, n = 2, and in triglyme n = 3, etc. Kinetics of thermolysis of p-tert-butylbenzenediazonium tetrafluoroborate in dichloroethane at 50 °C were followed by UV spectroscopy, and the effects of adding in turn ten equivalents of each of a series of glymes in which n = 2, 3, 4, 5, 6, 7, 8, 9 or 10 were observed. Little change was observed until n = 5 when the decomposition rate constant was observed to fall, showing increased stabilisation. For the next value in the series the rate constant decreased again until at n = 7 the rate rose sharply and then fell again.

An explanation of these values was obtained from the study of models which showed that the structures approached the form of a ring and that in heptaglyme all eight oxygen atoms lie in a plane without significant van der Waals repulsion or angular strain. In octaglyme, repulsion and strain exist in any conformation allowing nine oxygen atoms to lie on a plane within a pseudo-cyclic cavity. In nonaglyme and decaglyme, a pseudo-cyclic cavity is formed by eight of nine oxygen atoms and the others stand in an arm passing over one face of the cavity. In order to assess the effect of glymes with even larger molecules, experiments were made with the dimethyl ether

of Carbowax 1000, a polymer with structure $MeO(CH_2CH_2O)_{22-23}Me$, which gave a decomposition rate constant about half that of decaglyme. Although incorporation of 18-crown-6 ether was even better at promoting stability, the results on ethers of Carbowax are of interest because of their potentially lower cost.

1.9 INVESTIGATIVE STRATEGY

The importance of diazo compounds to the operation of positive and negative lithographic printing plates has been explained above. In order to improve the lifetime of printing plates it is first necessary to investigate the processes that occur during plate and plate coating aging. Once the major processes and chemical reactions that give rise to the observed deterioration in performance have been identified, these can be examined in further detail.

Given that lithographic printing plates and the coatings from which they are manufactured contain a complex matrix of chemicals, the initial investigations concentrated on simple one or two component systems. These were examined after they had decomposed at various elevated temperatures. The experiments were designed so as to provide sufficient data to be able to elucidate the reaction mechanisms that lead to the production of the decomposition products observed.

It was intended to begin with simple monomeric diazo compounds in simple matrices and then to extend the work to an understanding of the behaviour of monomeric and polymeric diazo formaldehyde condensates in full coating systems.

Once an understanding of the reaction mechanisms had been obtained, the work was to be directed towards the overall goal of extending the lifetime of the coating during plate manufacture and of the printing plate produced. It is of course equally important that any changes in coating formulation do not detract from the photoreactivity of the coating system. To this end the

effect of photochemical as well as thermal decomposition was investigated.

The investigative strategy can be summarised as follows:

1. Examine plates and coatings that contain monomeric diazo compounds for factors influencing the rate of decomposition.
2. Analyse plates and plate coatings for degradation products formed under controlled conditions.
3. Investigate the effects of heat on diazo compounds in isolation.
4. Extend this treatment to thermal decomposition in simple matrices of compounds found in lithographic plates and coating solutions.
5. Using a range of diazo compounds develop mechanistic guidelines for the processes involved.
6. Based on the information gathered, attempt to improve the thermal stability of the diazo system by use of certain coating additives and elimination of commonly encountered impurities.
7. Extend the scope of the investigation to photochemical decomposition in lithographic plate systems and to polymeric diazo compounds of the type used in negative working plates.

2 RESULTS AND DISCUSSION

2.1 INITIAL INVESTIGATIONS

Monomeric diazo compounds are used in positive working plates. Plates and plate coatings of this type were therefore chosen for initial investigation. A simple plate formulation consisting of a cresol novolak, diazo ester, colour change dye and acid release diazonium salt was used.

The complete formulation was :

Cresol novolak	75% w/w
Diazo ester	20% w/w
Colour change dye	4% w/w
Diazonium salt	1% w/w

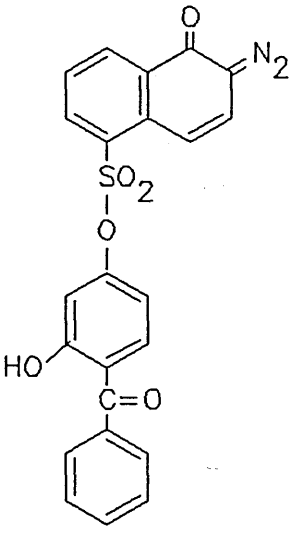
Cresol novolak is a cresol formaldehyde condensate as shown earlier in structure (6). The resin used in this work is a commercially available grade from Bakelite, Germany.

Some printing plates incorporate the quinone diazide as an ester of the novolak polymer. Preparing the ester using a diazo acid chloride will preferentially react with the monomers in the novolak polymer. This has the advantage of removing residual free cresols left over from the condensation reaction. This is preferable in commercial plates as the presence of cresols can be detected as a characteristic smell during plate processing. Such odours represent only low concentrations of cresols but are perceived as an avoidable health hazard by print customers.

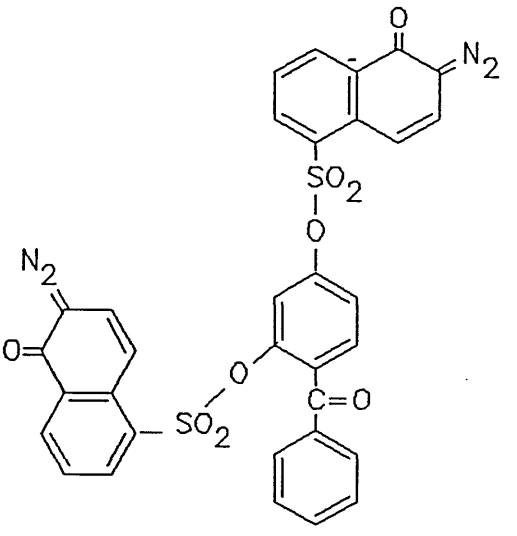
For this work the added complication of analysing the range of polymer decomposition products that would be formed is a major drawback, hence the simple mixture rather than novolak ester has been used.

The diazo ester is a 1,2-naphthoquinone diazide-5-sulphonic acid ester of 2,4-dihydroxybenzophenone with the structure given below (16) . The ester is primarily the bis ester but a small amount (about 15%) of the mono

ester is also present depending on the relative amounts of reactants used.



Mono Ester

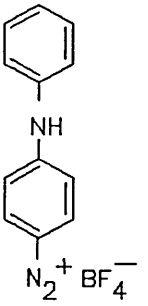


Bis Ester

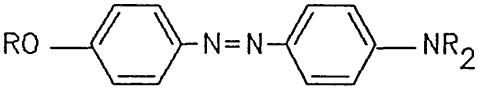
(16: Mono and bis 1,2-naphthoquinone diazide-5-sulphonic acid esters of 2,4-dihydroxybenzophenone)

The selection of the acid release agent is of particular importance as it not only has to fulfil its functions as an acid release, but also act as a model for the negative working diazo formaldehyde condensation polymers used in negative plate systems. The obvious choice is diazo diphenylamine because the polymeric diazodiphenylamine-formaldehyde condensate is widely used in negative plates. It is available with a variety of counterions such as HSO_4^-, BF_4^- and PF_6^-. Although the bisulphate salt will not liberate a Lewis acid on exposure, it is of use for preparing salts with alternative counterions. The BF_4^- salt (17) was chosen for initial investigation .

Finally, the colour change dye could be one of many azo based dyes that undergo an acid/base colour change. The selected dyestuff had the following generalised structure (18):

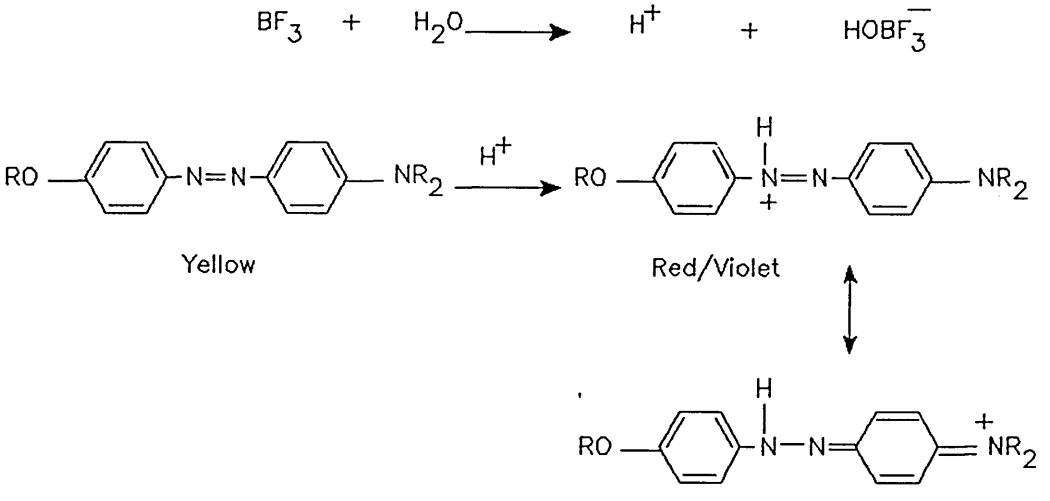


(17: Diazodiphenylamine tetrafluoroborate)



(18: Generalised structure for acid/base azo dye)

On exposure the diazo ester reacts to give an indene as in schemes 1 and 4 above, and the diazodiphenylamine salt decomposes to generate the BF_3 Lewis acid as in scheme 5. The colour change dye becomes protonated to give a bathochromic shift to absorption at longer wavelengths as follows (scheme 17).



(Scheme 17: Colour change reaction with Lewis acid)

The coating solutions used for commercial on-line printing plate manufacture usually have about 10% solids content in a quick drying solvent such as acetone. Single

preparations of experimental plates can be made using a whirler. This is a rotating disc similar to a large record deck. If a piece of aluminium plate substrate is fixed to the disc and rotated at high speed, plate coating solution poured onto the centre will be flung outwards to give an even coating film. This is explained in detail in section 3.10.

For the initial investigations a coating was prepared according to the formulation given above at 10 % w/v solids content in acetone. A portion of this was diluted by 50% with acetone to give a solution of whirling strength and an experimental plate prepared. After whirling, the plate was heated in an oven at 100 °C for 5 minutes to simulate the drying heaters used to evaporate off residual solvent in commercial production.

Both the plate and the 10% coating were analysed when fresh for diazo ester, diazonium salt acid release, colour change dye and coating weight (in the case of the plate) or solids (in the case of the coating). The chemical analysis utilised high performance liquid chromatography (HPLC) to reduce the possibility of interference between the various similarly coloured diazo and dye species and their decomposition products (as detailed in sections 3.4 to 3.6).

The 10% w/v coating solution was divided into three 50 ml. portions which were stored at 5 °C in a refrigerator, and at 30 and 40 °C in ovens. These were to assess the effects of cold storage compared with those at the operating temperature of commercial coating machines and at a more elevated temperature for accelerated aging. The whirler produced experimental plate was also analysed fresh and after storage under the same conditions as the coating.

The following results were measured after 7 days storage expressed as a percentage remaining of each analyte compared to the value in the fresh sample.

Table 2 : Plate analyses after 7 days storage at 5, 30 and 40 °C (% initial values).			
Temperature	Diazo ester	Diazonium Salt	Dye
5 °C	99	99	100
30 °C	95	66	98
40 °C	88	48	98

Table 3 : Coating analyses after 7 days storage at 5, 30 and 40 °C (% initial values).			
Temperature	Diazo ester	Diazonium Salt	Dye
5 °C	98	99	99
30 °C	94	75	96
40 °C	91	62	97

There are many similarities in the two sets of results. Firstly the colour change dye is essentially stable at storage conditions of up to 40 °C. The diazo ester loses about 10 % of its initial value at 40 °C. The most unstable component is the diazonium salt which is a diazo diphenylamine based acid release agent.

What effect do these losses have on plate performance? The plates were exposed for a standard exposure of 30 seconds on a printing plate exposure frame and developed through commercial positive developer (Posidev from Du Pont Howson). The plates after exposure but before development showed a noticeably reduced colour change after 30 °C storage (34% loss of acid release) and very poor colour change after 40 °C storage. However both plates developed cleanly. The acceptable development is due to the relatively small loss of the diazo ester which, with the novolak, is the main alkali soluble portion of the formulation.

The decomposed coatings were tested in an identical fashion. They were diluted to 5% with acetone and used to

prepare whirled plates. It was noticeable that there was some darkening of the whole plate before exposure, particularly for the plate from the 40 °C stored coating. This is probably due to pre-triggering of the colour change due to Lewis acid release during decomposition. On drying off the coating the colour reverted to close to that of fresh plate. On exposure the loss of colour change was only just noticeable for the plate from the 30 °C coating (25 % loss) but was clearly apparent for the 40 °C coating. Again the plates developed cleanly.

In conclusion, it is the decomposition of the diazo diphenylamine acid release agent in both stored plates and coatings that gives rise to significant loss of performance in positive plate formulations. The lack of colour change becomes noticeable to the eye once the level of acid release has fallen by more than about 25% of the original level.

Changing the formulation to include more acid release agent so that there is sufficient remaining after storage to provide adequate acid to give a colour change is not a practical solution. Experiments showed that doubling the level of acid release entailed an increase in exposure time to give correct development. This is due to absorption by the acid release of some of the incident radiation that would otherwise be used to convert the diazo ester to the developer soluble indene carboxylic acid. This is because both absorb in the same part of the spectrum. (See absorption spectra Figure 3 below).

Also unless the decomposition occurs to the same extent every time there will be too much or too little acid released giving rise to an unacceptably inconsistent product. Finally the build up of acid release and decomposition products are likely to give a pre-triggered colour change as shown in the coating decomposition experiments.

These initial experiments provided a basis for choosing what species to investigate more fully so as to

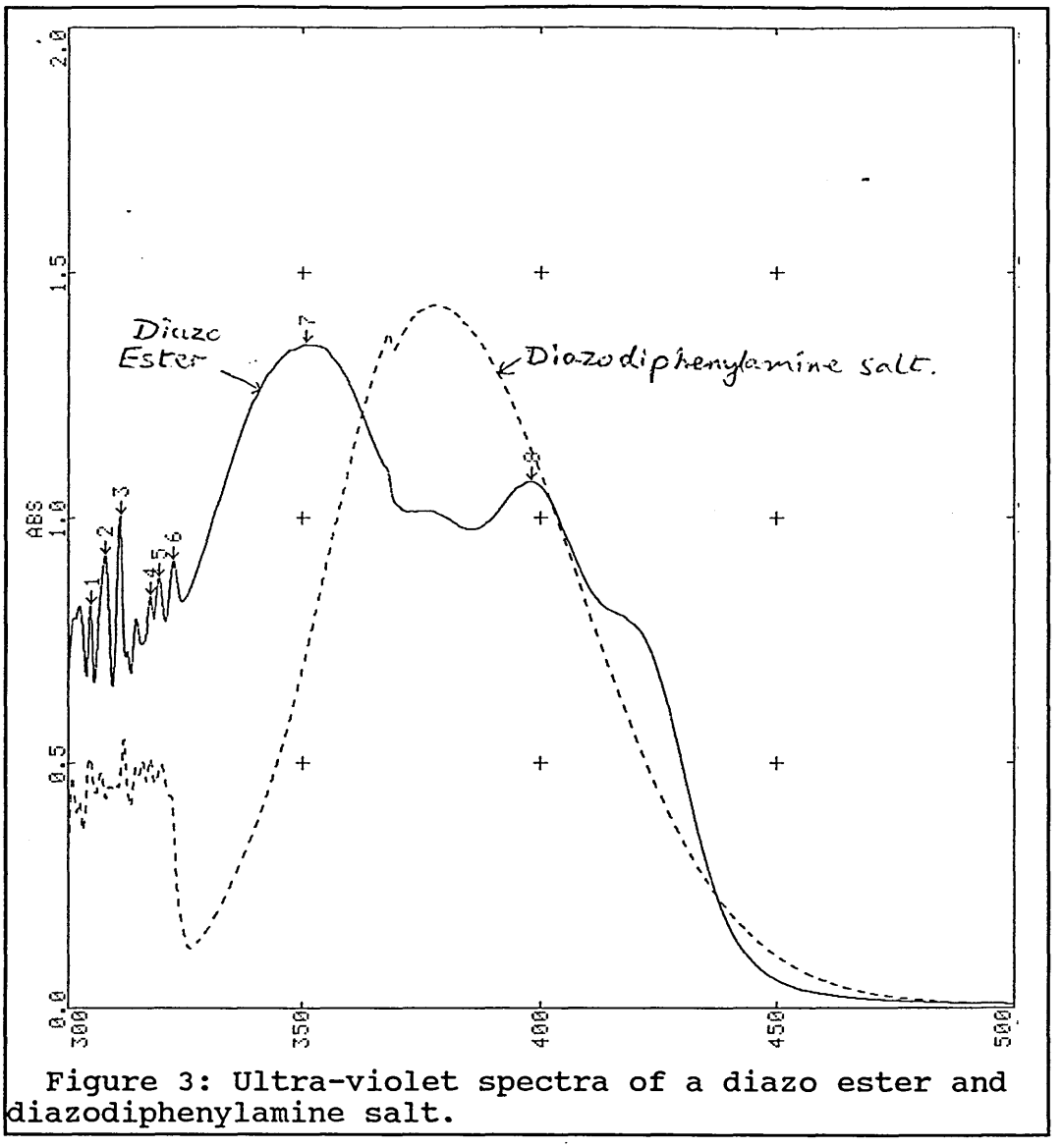


Figure 3: Ultra-violet spectra of a diazo ester and diazodiphenylamine salt.

obtain the desired stability improvement: The finding that diazodiphenylamine decomposition is apparently the main cause of deterioration in plate properties on storage together with the fact that the same compound is used as a cationic initiator for negative plates, and also its use as a negative working diazo resin in the form of formaldehyde condensate, make it the obvious choice for detailed investigation.

2.2 PRELIMINARY EXPERIMENTS ON DIAZONIUM SALT COATINGS

2.2.1 Factors affecting decomposition rate: cresols and novolaks

As has already been shown in section 2.1, the most unstable component of positive working lithographic plate formulations is the diazodiphenylamine salt used as an acid release agent. What factors are influencing this decomposition? If these can be identified their control should provide some improvement in stability.

The most obvious factor is temperature. It was decided to simplify the experiment as much as possible by concentrating on the diazodiphenylamine salt in isolation, away from the influence of the other chemicals in the coating. An experiment was set up with the diazodiphenylamine BF_4^- salt stored as a solid and as a solution in acetone at the concentration present in lithographic coatings. The latter was contained in a small brown glass bottle sealed with a solvent vapour proof screw top. Surprisingly, after 7 days storage at 40 °C there was very little decomposition in either the solid or the solution. The solid had decomposed by 2% and the acetone solution by 4%, neither result being anywhere near the 38% decomposition observed from a full coating solution (section 2.1).

Clearly some factor in the coating solution was affecting the rate of decomposition. This was easily assessed by preparing solutions that only contained portions of the coating formulation. Thus a stock solution of diazodiphenylamine was divided into four portions to which were added each of the other coating components separately. After one week stored under the same conditions as the diazo only solution above, the solutions containing the naphthoquinone diazide esters and the colour change dye had only decomposed by 4 and 8% respectively. The diazodiphenylamine in the cresol novolak solution had decomposed by 33%.

This is as might be expected given that the novolak comprises 75% of the solids of the coating. The decomposition is clearly accelerated compared to diazodiphenylamine solutions alone. Chemically cresol and the novolak prepared from it were expected to behave in a similar fashion. As any analysis of the decomposition products might well include products where the diazodiphenylamine had reacted with the novolak, the next step was to carry out a stability comparison with diazodiphenylamine BF_4^- salt in p-cresol and cresol novolak solutions. If these showed the same or similar levels of decomposition it would be a simpler task to analyse the cresol solution for decomposition products than that containing the condensation polymer.

However after 7 days at 40 °C as before, the solution containing p-cresol had lost only 18% of the diazodiphenylamine compared to 35% from the cresol novolak solution. This prompted a comparative investigation of other cresols and alkyl hydroxybenzenes to try to simulate the effect observed with novolak.

The decomposition experiments were set up with 10% w/v of the alkyl hydroxybenzene and 0.25% w/v of diazodiphenylamine BF_4^- in Analar acetone in 50 ml. brown glass vapour sealed bottles. These amounts were chosen so as to correspond approximately to the proportions found in positive working coatings. It was found necessary to thoroughly rinse out the bottles used to carry out the tests. This was in spite of using new bottles for the test solutions. These were found to contain some alkaline residues which could be removed by washing first with distilled water and then with Analar acetone. The samples were tested after 6 days storage at 40 °C in a laboratory oven. At the end of this period the solutions were analysed by HPLC as in method 3.6.

Results were reproducible to +/- 3% decomposition. The following average decomposition results from repeat tests were obtained.

Table 4 : Diazodiphenylamine decompositions after 6 days storage at 40 °C in 10% w/v solutions of various alkylhydroxybenzenes.

Diazodiphenylamine in acetone incorporating:	% Decomposition
No additions	5
Cresol novolak	33
Phenol	14
o-Cresol	22
m-Cresol	22
p-Cresol	14
o-Dihydroxybenzene	37
m-Dihydroxybenzene	14
p-Dihydroxybenzene	24
2-Ethylphenol	11
3-Ethylphenol	10
4-Ethylphenol	10
2-tert-Butylphenol	30
4-tert-Butylphenol	18
Di-tert-Butylphenol	32
2,3 Dimethylphenol	32
2,4 Dimethylphenol	36
2,5 Dimethylphenol	28
2,6 Dimethylphenol	35
3,5 Dimethylphenol	18
1,2,3 Trihydroxybenzene	45
1,2,4 Trihydroxybenzene	100

The manufacturers of the cresol novolak used in this and other tests were contacted to try to find out if they had any data on the cresols blend used in the manufacture of the novolak. They had limited information dictated by the resolution of the gas chromatograph and column used for the analysis. A typical analysis of the cresols blend used is as follows:

Table 5: Mixture of alkylhydroxybenzenes used in the manufacture of cresol novolak (results as supplied by the manufacturers).	
Alkyl hydroxybenzene	% w/w
m-Cresol combined with p-cresol	72.2
2,4 Dimethyl phenol combined with 2,5 dimethyl phenol	16.0
3,5 Dimethyl phenol combined with 3-ethyl phenol and 4-ethyl phenol	5.3
2,6 Dimethyl phenol	2.0
o-Cresol	1.9
2-Ethylphenol	1.5
2,3-Dimethylphenol	0.8
3,4-Dimethylphenol	0.2
Phenol	0.1
TOTAL	100.0

No more detailed information was available except that the meta isomer made up the bulk of the 72.2 % mixed meta and para isomers.

Although these figures are interesting in giving a comparison with the decompositions observed in the presence of the various alkylhydroxybenzenes, they have little bearing on the residual cresols in the novolak. These were measured by gas chromatography in two batches used for the decomposition experiments and were as follows:

Table 6: Phenolic monomers measured by gas chromatography in cresol novolak resins.		
Monomer	% w/w in Bx 33	% w/w in Bx 39
m- and p-cresol	3.3	2.4
2,4 dimethylphenol	1.0	0.6
o-cresol	0.2	0.1

Reference to table 4 indicates that whereas the cresols only give 14-22% diazo decomposition, the 2,4

dimethylphenol does give more decomposition at 36 %. However these values were obtained for 10 % w/v solutions of the alkylhydroxyphenols concerned. The levels of total free alkylhydroxyphenols in the two typical batches above are only 4.5 and 3.1 % w/w of the resin respectively. This is insufficient to explain the significantly worse level of decomposition observed for the novolak compared to its parent cresols.

Overall several interesting results come out of this work:

1. The diazodiphenylamine salt is comparatively stable in acetone alone. The decomposition is accelerated to varying degrees by alkyl hydroxybenzenes.

2. The cresol novolak polymer solution gives increased diazodiphenylamine decomposition compared to the cresols from which it has been manufactured.

3. Substituents in the phenol have a marked effect on the rate of decomposition. It is noteworthy that:

(a) All the ethyl phenols give lower diazodiphenylamine decompositions than the corresponding methylphenols (cresols).

(b) In most cases, cresol solutions give lower diazodiphenylamine decompositions than dialkyl substituted phenols.

(c) The effect of mono to di- to tri- hydroxy groups is less clear. There is an overall change from the fairly stable phenol containing solution (14% decomposition) to the very unstable 1,2,4 trihydroxybenzene (100% decomposition), but it is unclear why the 1,2,3 isomer should only give 45% decomposition.

This latter point was investigated further as a possible explanation for the difference in the effects of cresol novolak compared to the corresponding monomeric cresol. It was postulated that the increased decomposition observed in the presence of the novolak might be due to an

increased hydroxy value. The hydroxy values were measured with the following results:

m-cresol hydroxy value 15.5 % w/w.

cresol novolak hydroxy value 10.2 % w/w.

(The theory level for m-cresol is 15.7 % w/w.)

From the clear result that the novolak hydroxy value is considerably less than that for the cresol, any correlation between diazonium decomposition and hydroxy value does not explain the increased diazonium decomposition in novolak.

Having shown the variations produced by solutions containing varying types of alkylhydroxybenzene, it was thought appropriate to investigate in a similar fashion the effects of various commercially available novolaks prepared from different alkylhydroxybenzenes. These were investigated at 10% solutions in Analar acetone containing 0.25% w/v diazodiphenylamine BF_4^- salt (DDBF4).

Table 7 : Diazodiphenylamine decomposition levels measured after 7 days at 40 °C in 10% w/v solutions of commercial phenol and cresol formaldehyde condensates (novolaks).

Novolak	Source	% Decomposition ($DDBF_4$ 7 days 40 °C)
Octyl Phenol	Featley Chem.	72
Cresol	Featley Chem.	24
Cresol	Alnovol	30
Phenol	Bakelite	16
Cresol (low M.W.)	Bakelite	26
Cresol (high M.W.)	Bakelite	32

The high and low molecular weight Bakelite batches represent the standard grade of resin, selected to represent the specification range. The "high" molecular weight batch has a molecular weight only 25% higher than the "low" molecular weight batch.

These resin results show that the cresol novolaks from different sources behave in a broadly similar

fashion. The two noticeable results are that the octyl phenol novolak gives worse stability and the phenol novolak slightly better stability. The phenol novolak result corresponds to the improved stability seen for phenol compared to cresol monomers in the table above.

Novolak Purification

The different effects on the stability results of novolaks and the parent cresols were investigated further by attempts at purification of the resin. It is incorrect to think of novolak resin as consisting of high molecular weight polymer with a few percent remaining monomeric cresols/xylenols. A more accurate picture is that shown by gel permeation chromatography below (figure 4). This shows a separation according to the size of the molecule in solution- the hydrodynamic volume.

This technique is used to measure the molecular weight of soluble polymers and is particularly useful for rapid semi-quantitative comparisons. An analysis only takes about a quarter of an hour, and gives accurate quantitative comparisons. The molecular weights are not absolute, however, as the separation is based on the size in solution, which is only partially determined by molecular weight. Other factors such as the degree of solvation and interactions with the mobile and stationary phases will also have an effect. The column system was calibrated with a series of polystyrene narrow dispersity molecular weight standards.

The separation, as explained in more detail in the experimental section, is the reverse of a sieve effect. Thus the larger molecules elute first, followed by those of medium molecular weight and finally low molecular weight oligomers and monomers. As explained in section 3.11, the calibration is based on the logarithm of molecular weight standards plotted against retention time. Small differences in retention signify comparatively large differences in molecular weight.

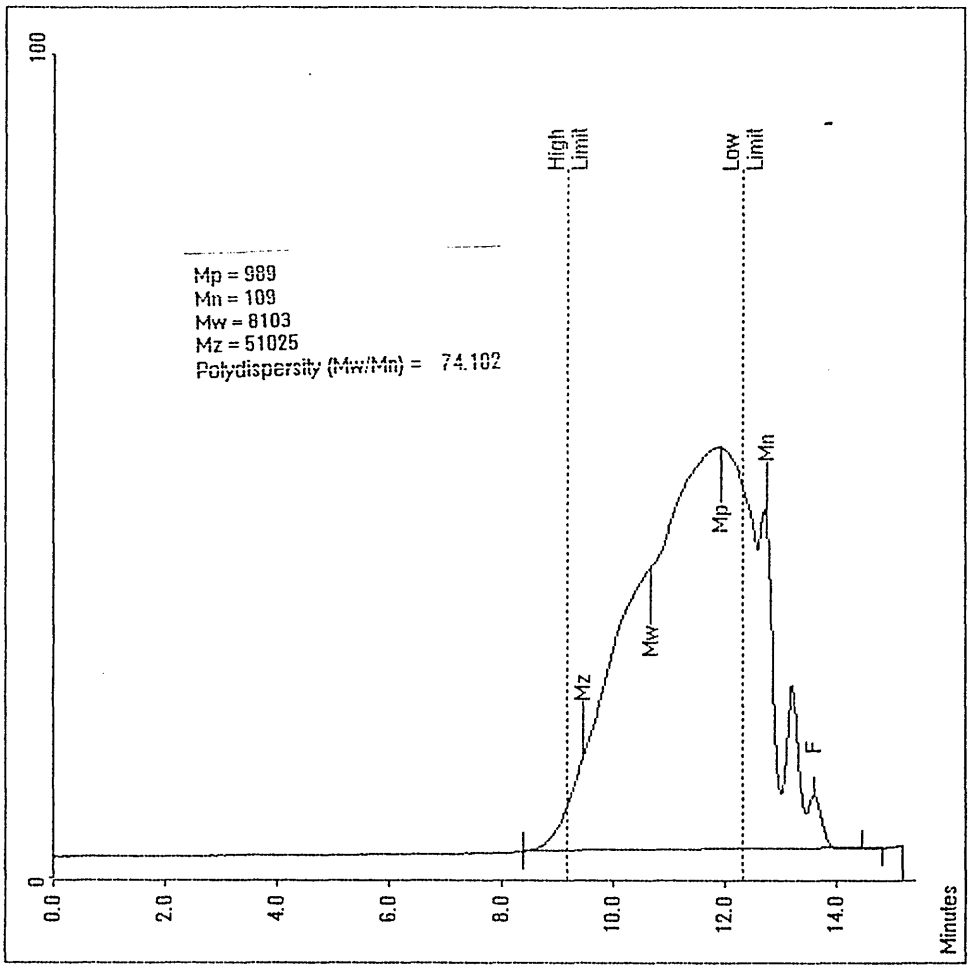


Figure 4: Gel permeation chromatogram of cresol novolak resin using two PLGEL mixed pore size columns.

The cresol novolak gives a broad molecular weight distribution. Compared to the polystyrene calibration, the weight average molecular weight is 8103, and the polydispersity (an indication of the broadness of the molecular weight distribution) is 74. This latter figure is probably inaccurate due to the interference by monomeric components in the determination of the number and weight average molecular weights used in its calculation. The most prevalent component at the highest part of the chromatogram is at a molecular weight of 989 (the Mp).

To attempt to assess what factors in the novolak were influencing diazonium salt decomposition, an experiment

was set up to fractionate the novolak polymer with the aim of using the fractions in stability determination tests. The fractionation was carried out by first dissolving about 20 gms. of novolak in 500 mls. Analar acetone. The dissolution took about two hours in a beaker with a stirrer. The solution was filtered and about 3 % of the novolak filtered off as insolubles. Cresol novolak is only sparingly soluble in methanol. Methanol was added dropwise from a Pasteur pipette. Eventually some of the novolak began to precipitate out. Initially an attempt was made to filter this out but this blocked the filter with a sticky mass of novolak. A preferable method was to remove the sticky solid with a spatula. More methanol was added and the next fraction removed. Finally the remaining methanol/acetone solution was evaporated down on a rotary evaporator. The fractions were dried down further in a vacuum oven at 40 °C overnight. This gave three fractions which were analysed by gel permeation chromatography under the same conditions as the untreated parent novolak shown above (Figure 4). The results are shown below (Figures 5-7).

The molecular weight fractions are described as high, medium and low molecular weight (MW) fractions. Results in terms of MW are summarised in the following table.

Table 8: Cresol Novolak molecular weight fractionation results

Fraction	MW	%
Parent (untreated)	8100	-
High molecular weight	231000	15
Medium molecular weight	13100	63
Low Molecular weight	760	19
Total		97

The chromatograms include the limiting molecular weights used in the polystyrene calibration as explained in greater detail in Section 3. The calibration is

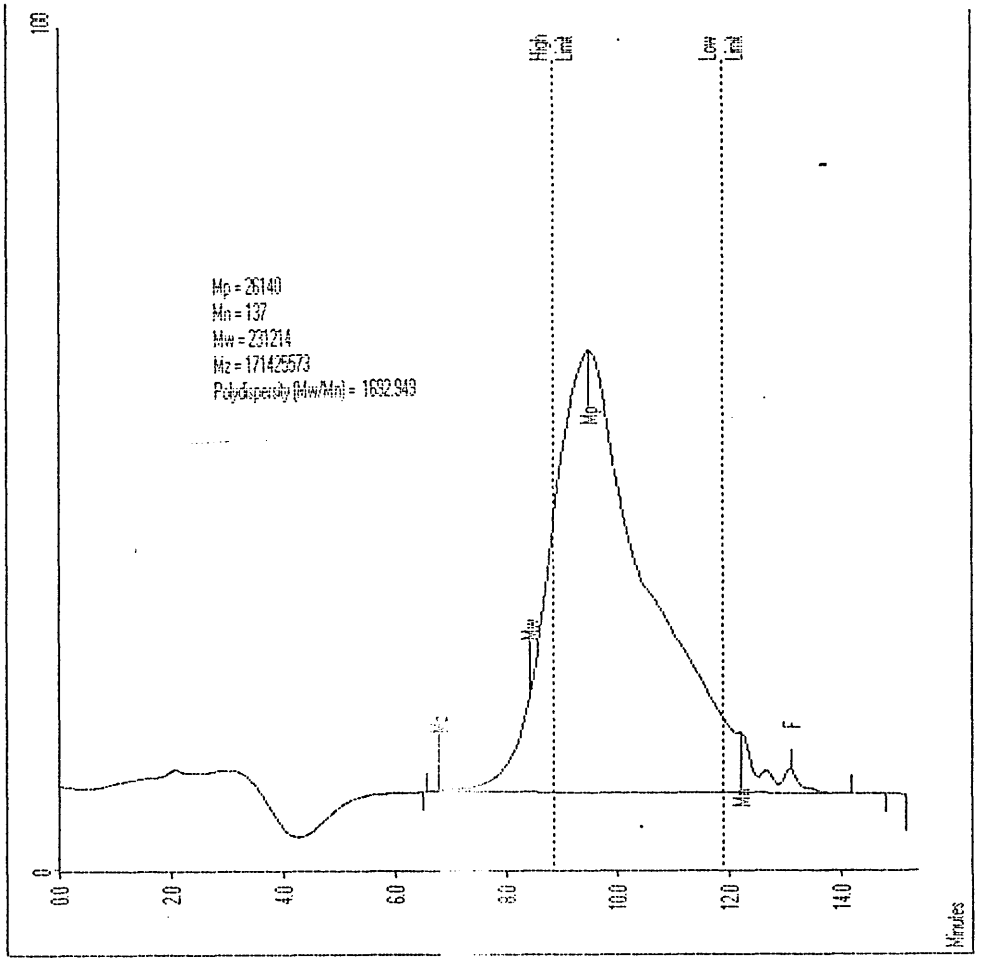


Figure 5: Gel permeation chromatogram of the high molecular weight cresol novolak fraction.

extrapolated for any portion of the sample profile outside the calibration region. With the third order polynomial generated for the calibration, extrapolation will give acceptable values for the portion of the chromatogram at the low molecular end but values that are too high for the high molecular weight portion outside the calibration. For this reason the average Mw figures quoted in the table above are likely to be accurate for all except the high molecular weight fraction. Its average molecular weight is probably considerably below the 231000 quoted above. Nevertheless it is clear that a very effective separation has occurred giving a much wider molecular weight variation than that encountered from batch to batch differences within the same grade of novolak.

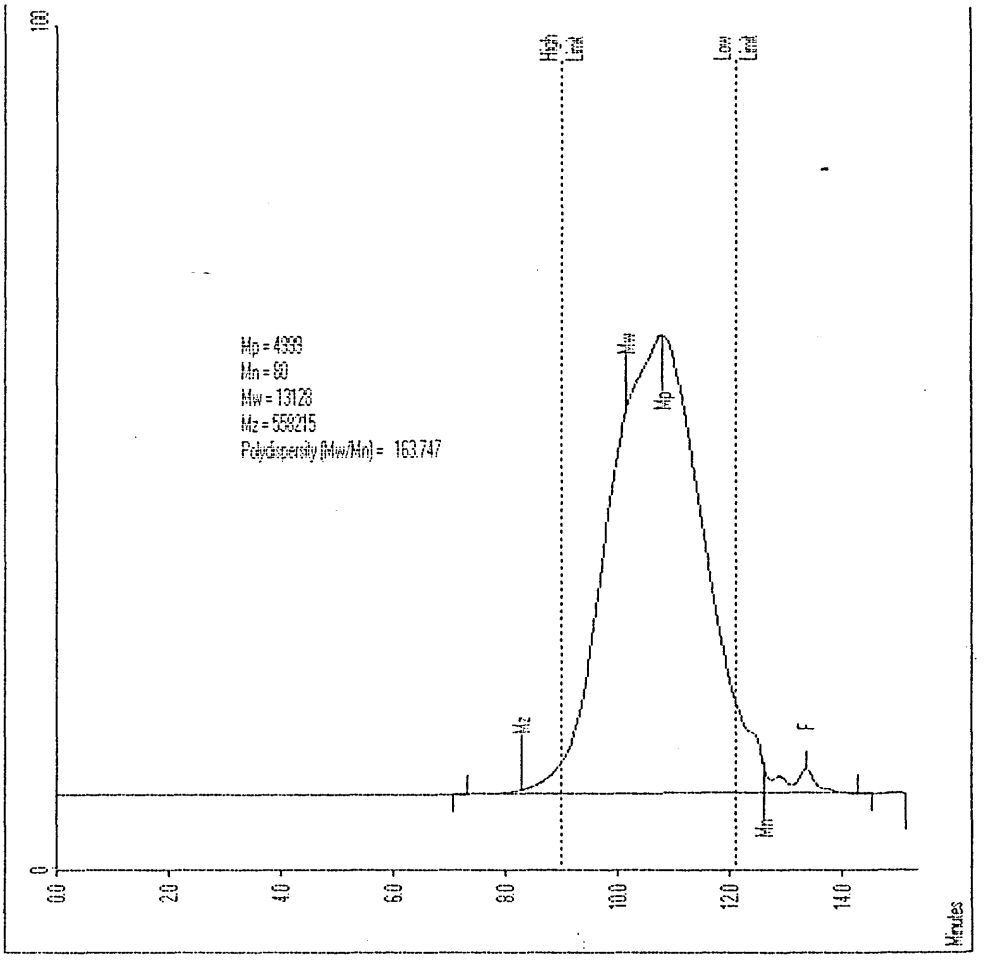


Figure 6: Gel permeation chromatogram of the medium molecular weight cresol novolak fraction.

The original sample and the three fractions were used for a.decomposition trial using diazodiphenylamine tetrafluoroborate. This used the novolaks at 10% w/v and the diazonium salt at 0.25% w/v in Analar acetone. The stability test on the diazonium salt took place over 10 days at 40 °C with the following results.

Table 9: Effects of novolak fractions on diazodiphenylamine salt decomposition.

Novolak fraction	% Decomposition
Untreated Novolak	39
Low molecular weight novolak	36
Medium molecular weight novolak	32
High molecular weight novolak	29

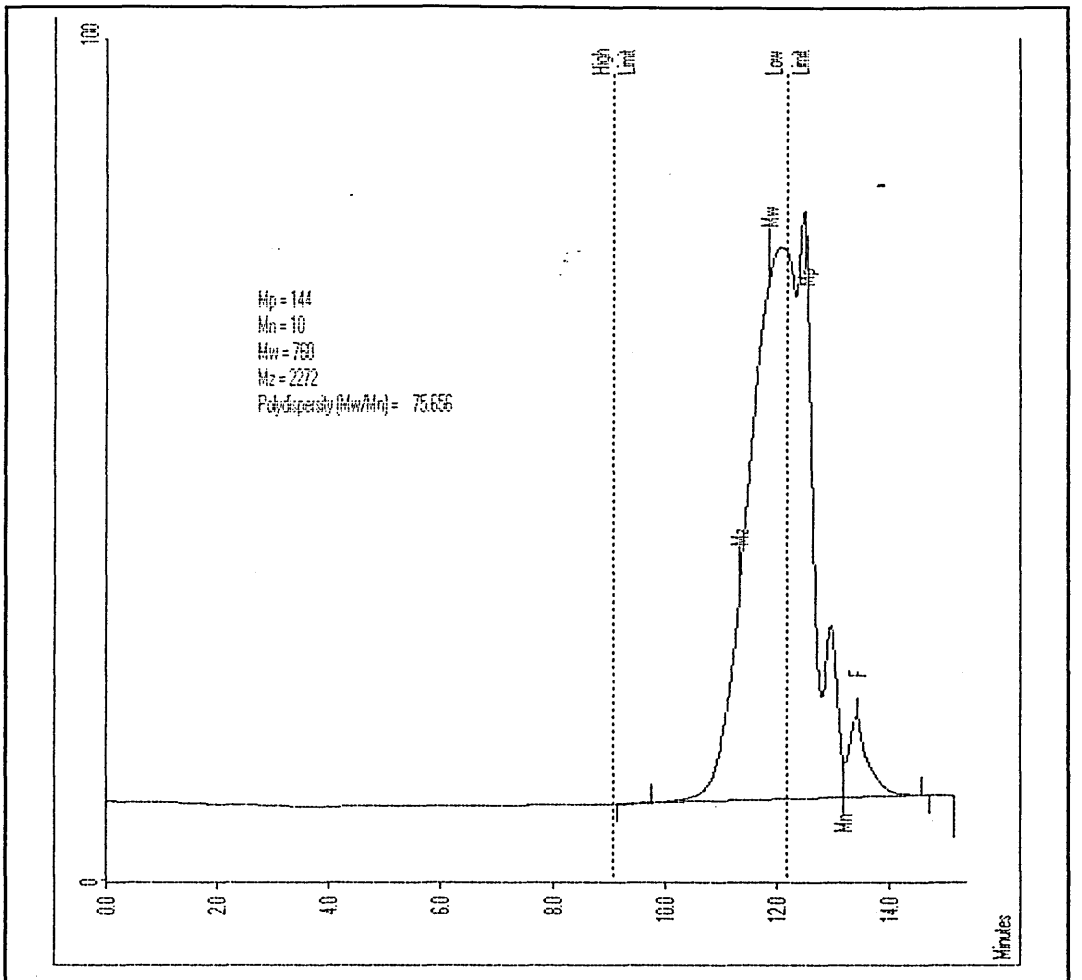


Figure 7: Gel permeation chromatogram of the low molecular weight cresol novolak fraction.

The results are very interesting in that they demonstrate the first possibly effective way of improving the thermal stability of diazonium salts in lithographic systems encountered during this investigation. The use of the high molecular weight resin has resulted in a significant drop in decomposition from 39 to 29 % under the conditions of this test. There is a gradual worsening of the diazonium stability as lower molecular weight resins are used. What is at first surprising is that none of the three resin fractions gives as poor a diazonium salt stability as the original resin from which they are made. If there is a trend towards poor stability with decrease in molecular weight, it would be expected that the lowest molecular weight resin would contain the highest concentration of destabilising compounds. Evidence

for the probable cause of this unanticipated result lies in the total recovery of the novolak fractions given in the table above. The recovery level was very high at 97 % of the initial resin weight. However, during the drying of the fractions any highly volatile components would have been lost as the methanol and acetone were removed. As will be shown in a later section, the influence of water on the rate of decomposition is particularly dramatic. The drying process will have removed water from all the fractions, hence none gave stabilities as poor as the original.

Having identified the chemical environment as being a critical factor in decomposition as well as temperature, an experiment was designed to put the temperature and time relationships on a more quantitative basis.

2.2.2 Time and temperature effects

In order to assess the relative rates of decomposition and provide further information on the difference in decomposition characteristics of cresol novolak and its parent cresol, a long term decomposition experiment was devised. This consisted of two 10% solutions of p-cresol and cresol novolak in Analar acetone, containing 0.25% diazodiphenylamine BF_4^- salt. As before the stability was carried out at 40 °C but this time over a period of 28 days, the solutions being analysed every few days.

The results are presented graphically in Figure 8.

This clearly demonstrates the increased rate of decomposition of diazodiphenylamine in the presence of novolak. It shows an initial period of two to four days during which decomposition is only slight, followed by a steady decomposition over the following 10 to 15 days, followed by a gradual levelling off in the rate of decomposition towards the end of the measurement period.

The results indicate an induction period at first before the decomposition route becomes established;

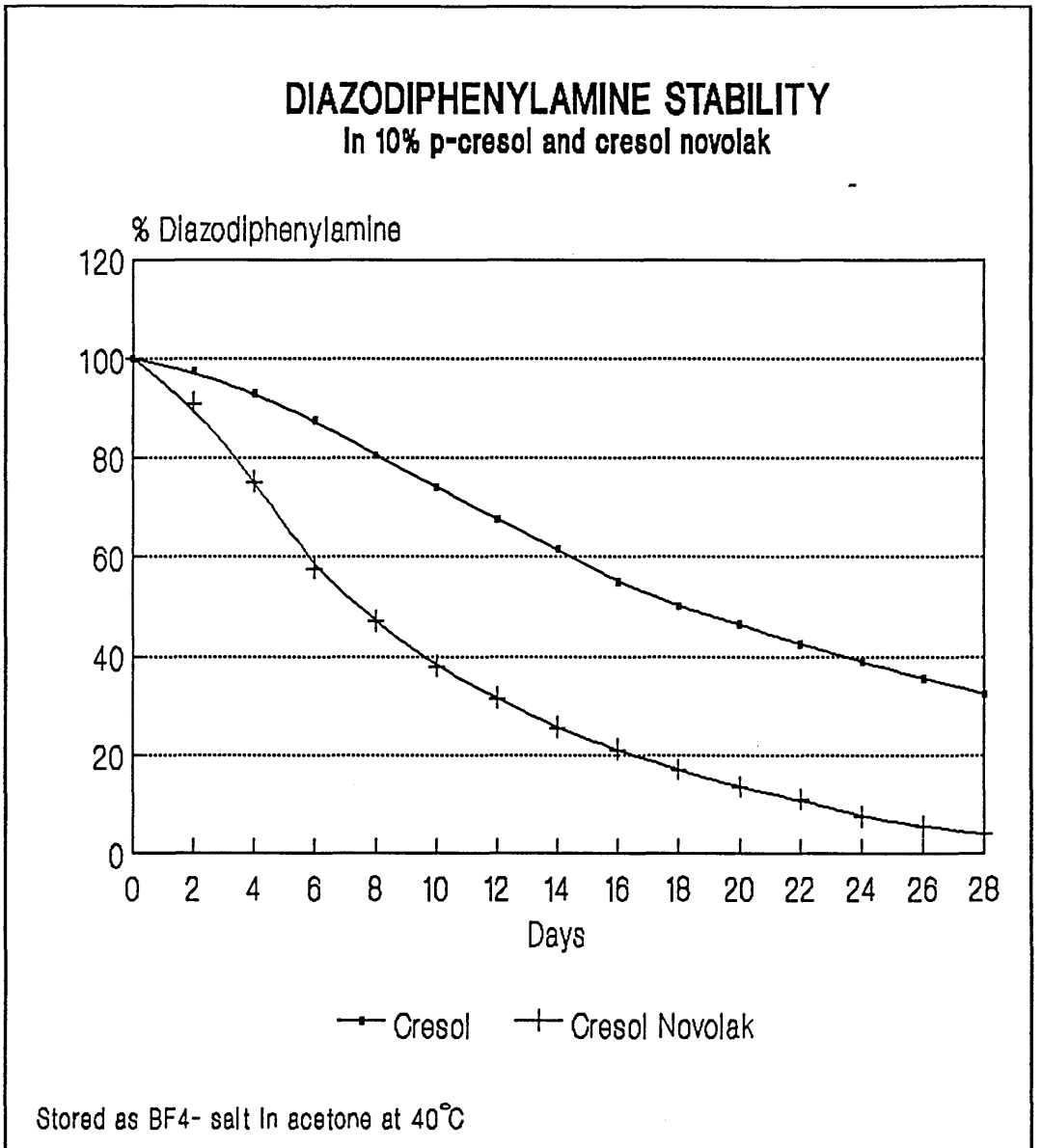


Figure 8: Diazodiphenylamine tetrafluoroborate stability in 10 %w/v cresol and cresol novolak solutions in acetone stored at 40 °C.

followed by steady decomposition until most of the diazodiphenylamine has been used up. Finally the decomposition rate begins to fall perhaps inhibited by the build up of decomposition products or due to the reduction in concentration of the reactants.

In the earlier series of experiments it had been shown that decomposition was much greater in the presence of 1,2,3 tri-hydroxybenzene, which is the readily available pyrogallol. The increased rate of decomposition

means that any effects can be observed over a shorter time. As some experiments were taking four weeks to complete, this is an important consideration. For the next and some future experiments pyrogallol was used in preference to cresol, although cresol was used in any experiments where a closer correspondence with plate behaviour was thought necessary.It is perhaps relevant to its effectiveness in the decomposition process that pyrogallol is a strong reducing agent and in alkaline solution readily absorbs oxygen.

Solutions were prepared in the now standard concentrations of 10% pyrogallol and 0.25% diazodiphenylamine BF_4^- in Analar acetone. The results are presented in Table 10.

Table 10 : The effects of temperature and time on diazodiphenylamine decomposition rate in 10% w/v pyrogallol in acetone.

Days Stored	% Remaining at temperature in °C				
	5	20	30	40	50
1	98	95	92	90	79
2	95	89	84	71	68
4	93	75	70	54	36
7	91	71	54	42	2
17	84	69	35	3	0

These results are more clearly expressed graphically in Figure 9 below.

The results show a similar relationship between the rate of decomposition of diazodiphenylamine and time as detailed in the Figure 8 concerning cresol and cresol novolak solutions. There is also the expected increase in decomposition with temperature. It is interesting that the levelling off of decomposition rate noted for cresol and cresol novolak solutions is particularly noticeable for the low temperature decomposition series of these tests. The 5 and 20 °C samples both undergo decomposition at a gradually reducing rate over the first seven days but

remain at a nearly stable level thereafter. Given that the concentration of potential reactants is relatively unchanged, this indicates some inhibition effect caused by the decomposition products.

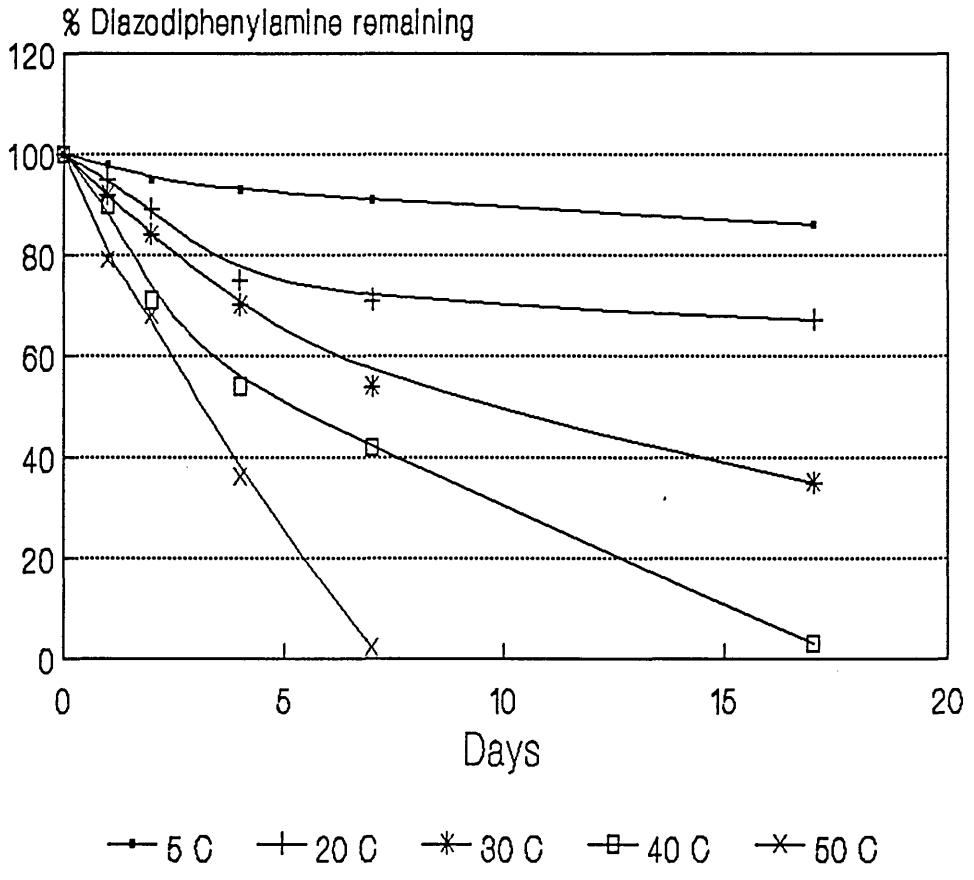


Figure 9: The effect of temperature on the rate of diazodiphenylamine decomposition in 10 %w/v pyrogallol in acetone solution.

2.2.3 Solvent and Water effects

As the solvent comprises the major component of the coating and test solutions, it would be expected to play a correspondingly major part in deciding the extent and mechanism of reaction. For this preliminary study, only solvents closely akin to acetone were considered.

Acetone is frequently used in lithographic coating preparations because of its excellent solvent strength, volatility, low toxicity and comparative low cost. The effect of other ketones in the same homologous series was first studied, using 1,2,3 trihydroxybenzene to give rapid decomposition. Results were compared after only two days:

Table 11 : The relative decompositions of diazodiphenylamine in a range of ketonic solvents containing 10% w/v pyrogallol.

SOLVENT	% DECOMPOSITION 2 DAYS 40 °C
Acetone	29
MEK	37
Pentan-2-one	34
Hexan-2-one	30

There is no significant difference or trend across the results. What was of more concern was that when the test was first carried out a result of 70% decomposition was obtained for the pentan-2-one. This was obviously out of step with the other results and some contamination was suspected. Analysis showed the presence of 1.3% v/v water. When a new batch of pentan-2-one was used, the above lower value for the decomposition was obtained. This served to demonstrate the dramatic increase in decomposition rate that is to be expected from even low levels of water in the system.

Subsequent review of other research papers has shown that this is a problem encountered by other workers[61a]. In the paper by Laali et al, which describes the first product analysis of diazonium salt decompositions in acetone, the results show clear evidence of contamination

by water. Over 60% of the decomposition products is the aryl phenol which is attributed to the presence of water in the D_6 acetone (NMR study). Similarly in the same paper the phenolic products produced in an acetonitrile solvent decomposition study were also attributed to contamination with water. No attempt was made to either quantify the water present or to try to eliminate it so as to give more meaningful results.

To obtain information on the likely effects of contamination by low levels of water on the rate of decomposition of diazodiphenylamine, a series of stability checks were carried out with controlled additions of water. The water content of the acetone used in the experiments described in this thesis was measured using the Karl Fischer method detailed in section 3.7.

The level of water in Analar acetone was found to be low at only 0.15 %w/v. The levels of additions of water and the percentage decompositions in test solutions containing 10 %w/v 1,2,3 trihydroxybenzene were as follows:

Table 12 : The effect of water on the decomposition rate of diazodiphenylamine in acetone containing 10% w/v pyrogallol.

% Added Water	% Water Measured	% Decomposition (7 days at 40 °C)
None	0.28	42
0.5	0.82	50
1.0	1.33	65
2.0	2.41	75
4.0	4.33	76

The water content of the solution without any water added has increased from the initial level of 0.15% in the acetone solvent, to 0.28% after the addition of the pyrogallol and the transfer of the solution from a beaker to the small brown Winchester for the stability trial. Measurements of the water content of the pyrogallol gave a result of 0.62% w/w, which would only contribute 0.06 % to

the increase in measured water content. The additional 0.07% is thought to be due to the acetone taking up low levels of moisture from the atmosphere and residual water on the glass apparatus surfaces. It was not found possible to significantly reduce the water content of the test solution by taking further precautions, while ensuring the glass containers were free of any residues that might contaminate the stability test solution.

Given that the stability test solutions contained a small but persistent level of water, two methods were used in an attempt to eradicate it. Firstly a molecular sieve. This is the use of dehydrated crystalline zeolites (alumino-silicates) that have unusual properties. The atoms are arranged in a definite pattern and the SiO_4 or AlO_4 tetrahedra are built into more complex structural units, often polyhedra. These polyhedra may have considerable cavities at their centres, while the stacking of the polyhedra can create new and larger cavities. Pores or windows open into and connect the cavities. For any particular type of such zeolite, these pores are precisely uniform in diameter; it is because of this feature that the name "molecular sieve" has been given to them, since the diameter of the pores determines the molecular sieve properties of each type, enabling it to adsorb selectively only those molecules which are of a suitable size and shape (i.e. capable of entering the pores). By sharing oxygen atoms, the polyhedra assume three-dimensional structures which often display remarkable rigidity and permanence though permeated by cavities interconnected by pores.

Normally these cavities contain water molecules, but when this water of hydration is driven off by heating, the crystal does not collapse or undergo rearrangement as do many other zeolites and hydrated materials. The physical structure of the crystals remains unchanged and robust. The range of molecular sieves produced by "Union Carbide" are described along with their applications in a booklet from BDH. Although no figures are quoted for acetone, for

other polar liquids such as ethanol on static tests the booklet indicates that it was possible to reduce the water contents to around 0.20 to 0.25%. However the figure for methanol was less good at 0.54%.

The sieve was added at 1% w/v to a solution prepared for a stability test containing diazodiphenylamine BF_4^- and pyrogallol in Analar acetone. It gave a cloudy solution . On analysing the solution when fresh the initial value was 28% below the theoretical figure. After storage for 7 days at 40 °C the level of diazodiphenylamine in solution had fallen to nearly zero. The low initial and final values showed that this is not a practical means of improving the stability, although the water content was reduced to 0.15%. The apparent poor stability is not entirely due to decomposition as analysis of the molecular sieve recovered from the stability test solution showed the presence of the diazo group. It is likely that adsorption of the diazodiphenylamine onto the sieve contributes to the poor stability results as well as worsened stability due to chemical effects of the sieve compound.

The second approach to reducing the water content was to use the compound dimethoxy propane. This has the useful property of reacting with water to give acetone and methanol.

$$(CH_3)_2C(OCH_3)_2 + H_2O \longrightarrow (CH_3)_2C{=}O + 2CH_3OH$$

(Scheme 18: Reaction between dimethoxy propane and water)

As acetone is already present as the solvent, adding dimethoxy propane should convert the water into methanol as the only additional compound. Potentially this might exert less of a detrimental effect on the rate of decomposition. Dimethoxy propane was added on a molar basis compared to the level of water found before its addition. It was added to the solution containing the pyrogallol in acetone but before the addition of the diazodiphenylamine, so as to reduce the possibility of reaction of dimethoxy propane with the diazo compound. The

water content was reduced from an initial measurement of 0.24% to 0.15%, but no further reaction took place. The solution stability results were disappointing, in that the stability was worse than that of a portion of the same solution to which no dimethoxy propane had been added. Without addition of dimethoxy propane, a decomposition of 39% was obtained compared to 52% for that with dimethoxy propane. This may be due to some unreacted dimethoxy propane causing increased decomposition of the diazodiphenylamine, or to the formation of methanol. As it was not a promising line of enquiry, no further work was done to elucidate the causes of the inferior stability with this compound.

Although the attempts at reducing the water content to zero had resulted in reduced stability because of the detrimental effects of the reagents used, it is nevertheless very important to make sure that water is eliminated from coating solutions and raw materials. The influence of water in solvents and other coating components is highly significant due to its effect on coating solution stability. Fortunately measurements of the water contents of the bulk acetone used in commercial plate manufacture revealed levels as low as that in Analar acetone (ie. below 0.3 %). Cresol novolak does contain a small amount of water which will make some contribution to the greater instability observed compared to the parent cresols. Measurements have shown that batches of cresol novolak have between 0.80 and 1.15 % water. This is due to the steam distillation that is carried out as part of the novolak purification process rather than that formed during the condensation reaction. Although this level of water is significant, it is not of overriding importance as the novolak is used at a level of 10 % w/v in the test solutions, and will therefore only contribute a further 0.1 % to the solvent water content.

The mechanism of decomposition of arenediazonium ions in water is the subject of recent research work[62]. This is an extension of work outlined in section 1.8.3, where two

intermediates were postulated to explain the exchange of labelled diazo nitrogen atoms with atmospheric nitrogen in heterolytic dediazoniation reactions. According to that mechanism (scheme 14) the first intermediate is a tight aryl cation-molecular nitrogen ion-molecule pair and the second is the free (solvated) cation.

The recent work compared the level of labelled nitrogen exchange from two diazonium salts in 2,2,2-trifluoroethanol (TFE), 1,1,1,3,3,3,-hexafluoropropan-2-ol (HFIP) and water. TFE and HFIP are solvents of very low nucleophilicity particularly in contrast with a strongly nucleophilic solvent like water. Dediazoniations were carried out in the presence of 300 and 1000 atmospheres of nitrogen. The results showed nitrogen exchange with the atmosphere of up to 16.5 % for the TFE and HFIP but values within the detection limit in the case of water. Earlier workers had shown up to 6% exchange using water as the solvent[63].

It should be born in mind as mentioned in reference 62 that the solubility of nitrogen at 25 °C and 300 atmospheres in HFIP, TFE and water is 4.94 mol/l, 3.05 mol/l and (only) 0.16 mol/l respectively.

The main reason for the back reaction (scheme 19) being observable for HFIP and TFE is their extremely low nucleophilicity which enables molecular nitrogen to compete more effectively as a nucleophile for the aryl cation.

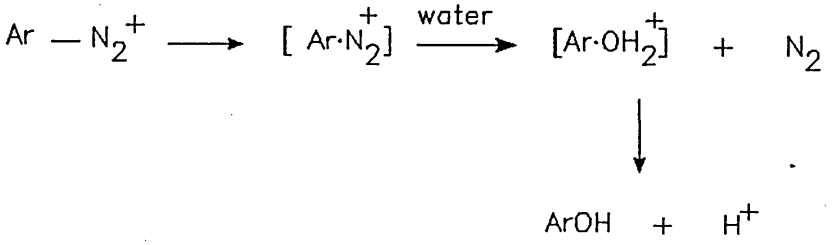
$$Ar^+ + N_2 \rightleftharpoons Ar - N_2^+$$

(Scheme 19: Reversible reaction between molecular nitrogen and an aromatic cation.)

Nevertheless this is a very unusual occurrence and represents the first evidence for a reaction of nitrogen with an organic compound in solution. When water is present, the reaction with water rather than nitrogen as a nucleophile is dominant. The nitrogen exchange results with water can be explained by postulating that the ion-molecule pair is trapped almost completely. The first

intermediate reacts so easily with the more nucleophilic species that the reaction of the second intermediate with nitrogen is not detectable. The first intermediate is, however able to return to the starting material, so a small amount of rearrangement is detected (as in reference 63). The exchange results reported do not necessarily mean that Ar^+ is not formed at all, only to such a small extent that it cannot be detected either by the back reaction with external nitrogen or the influence of molecular nitrogen concentration on the overall thermolysis rate.

Kuokkanen[64] investigated similar heterolytic reactions under pressure with TFE and other solvents. He came to the conclusion that there are two intermediates in reactions conducted in TFE and one in water and other solvents. However he also concluded that the intermediate is Ar^+. This conclusion is inconsistent with the observed diazo nitrogen Nα Nβ rearrangement. The rearrangement and the lack of influence of molecular nitrogen on the thermolysis rate or evidence for exchange reactions, indicates no reaction with the aryl cation but rather with the ion-molecule pair. The reaction with water is best represented as in scheme 20.



(Scheme 20: Reaction of ion-molecule pair with water)

2.2.4 Concentration Effects

Much of the work reported so far has been designed to simulate the effects in lithographic plate coating solutions. These contain a very large excess of cresol novolak or even of quinonediazide ester of novolak. To provide for comparison with earlier results and to increase the rate of decomposition, 1,2,3

trihydroxybenzene (pyrogallol) was used for these tests. Reduced levels of pyrogallol and reduced and increased levels of diazodiphenylamine BF_4^- were examined. (See table 13 below).

Table 13: The effects of relative concentration of diazodiphenylamine and pyrogallol on the decomposition rate of diazodiphenylamine.	
10% Pyrogallol, varying amounts of diazodiphenylamine BF_4^- (DDBF4).	
% w/v DDBF4	% DDBF4 Decomposition 40 °C 7 days
0.025	60
0.250	42
2.500	23
0.250 % diazodiphenylamine BF_4^-, varying amounts of pyrogallol.	
% w/v Pyrogallol	% DDBF4 Decomposition 40 °C 7 days
10.0	42 (Standard concentration)
1.0	6
0.1	4

These results demonstrate that the larger the excess of hydroxybenzene over diazodiphenylamine the larger the percentage decomposition. It is also clear that the effect of the hydroxybenzene on the rate of decomposition is only apparent at very large excess levels and that at anything like molar equivalent levels the effect on increased rate of decomposition is negligible. Any trace impurities in the hydroxybenzenes could be significantly influencing the rate of decomposition.

This was born out in the investigation reported in Section 2.2.1 where purified novolak was prepared and used for stability trials.

2.3 ANALYSIS OF DECOMPOSITION PRODUCTS

2.3.1 Introduction

It will already be apparent that the decomposition of diazonium salts is a complex process, subject to the effects of time, temperature, solvent conditions and presence of other chemicals in the matrix. Fortunately there is a correspondingly wide range of analytical techniques available to help elucidate the reaction mechanisms. The various alternative methods of tackling the analysis of the diazonium salts themselves are reviewed in a later section (2.4). The current section is concerned with the decomposition products that arise in diazonium salt stability tests under various controlled conditions.

Although some work was carried out on the complete plate formulation, the number of variables involved made a more detailed investigation of simpler systems a more appropriate methodology. This meant concentrating on the diazodiphenylamine BF_4^- salt in cresol solution and in solvent alone. The techniques used were partly dictated by what research equipment was available at Sheffield City Polytechnic and DuPont Howson although some work was also carried out at other establishments: for example elemental analysis, some mass spectrometry and some N.M.R. work.

Where possible, quantitative as well as qualitative results were obtained although some techniques are more appropriate for qualitative analysis only. Most of the quantitative data is as a result of analysis by the various chromatographic instruments particularly HPLC and GC but also the newer technique of ion chromatography (IC).

With gas chromatography (GC): the sample is injected into a flow of an inert gas, separated as it is flushed through a column at elevated temperature and the separated components measured by detectors such as the universal flame ionisation detector (FID) or by mass spectrometry (GC/MS).

Similarly for high performance liquid chromatography (HPLC): the sample is injected into a flow of solvent or solvent/water mixture and separated into its component parts as it passes through a column packed with an appropriate stationary phase. Detection is usually by on-line ultra-violet (UV) spectroscopy or by refractive index detection if there is only a feeble (UV) response. Both GC and HPLC are well established techniques of about 35 and 20 years standing respectively.

The use of ion chromatography is relatively new, having only become established in the last 5-10 years. As such it is still developing and new applications are continually being evolved. It is based on HPLC in that it uses a liquid eluent and pump system, and occasionally uses UV detection. More often the standard detector is on-line conductivity measurement because the sample components it is used for are ions. These cannot easily be analysed by other techniques, especially when mixtures of ions are present. IC in its original form used an aqueous based eluent, ion-exchange column packing and suppression of the eluent conductivity in a further column before detection by conductivity. In more recent versions it uses stationary and mobile phases more akin to those in HPLC with ion-pairing to extend the range of ions to organic as well as inorganic ones.

In this study the technique has been applied to the monitoring of BF_4^- and other counter-ions as the diazonium salts decompose. It is the first reported application of the technique to the complex anions present in conjunction with diazonium salts[65], and is a useful addition to the techniques that can be used in reaction mechanism elucidation. Other studies have concentrated on the fate of the diazonium cation to the extent that the destruction of the complex anion has been ignored.

2.3.2 Products detected in full plate formulations

Although the preliminary experiments had been carried out on coating solutions, this was in part due to the relative ease of analysis of the reasonably high concentrations of components present. However it is equally important to consider the decomposition products arising in printing plates, particularly as this reaction is commercially of great interest. There is also the risk that relying upon decomposition data from solution experiments may result in overlooking differences caused by the absence of coating solvent and the increased interactions between the solids of the coating formulation. Furthermore, a plate coating gives much greater opportunity for interaction with the air than the same coating as a solution in solvent.

The difficulty in analysing plates for decomposition products is not trivial. As the level of diazodiphenylamine salt is usually only about 30 mg/m^2, even if all this is decomposed to give one product, the amount present after removing the coating with solvent presents problems in detection by HPLC and conventional GC. However, the most sensitive detector is a mass spectrometer linked to a GC.

This combination was used as detailed in the experimental section. A whirled plate was prepared and heated at 105°C for 24 hours. The coating on a piece 50 cm^2 was removed by cutting the plate into strips and washing it off in 2 ml. of acetone. 0.5 microlitre of the acetone extract was injected into a gas chromatograph linked to an ion trap mass spectrometer. The total ion chromatogram gave only one extra peak compared to an unheated blank. Several other peaks were reduced in size, due to losses of solvents and some monomeric cresols from the novolak resin. The portion of the chromatogram containing the extra peak and its mass spectrum as shown in Figure 10.

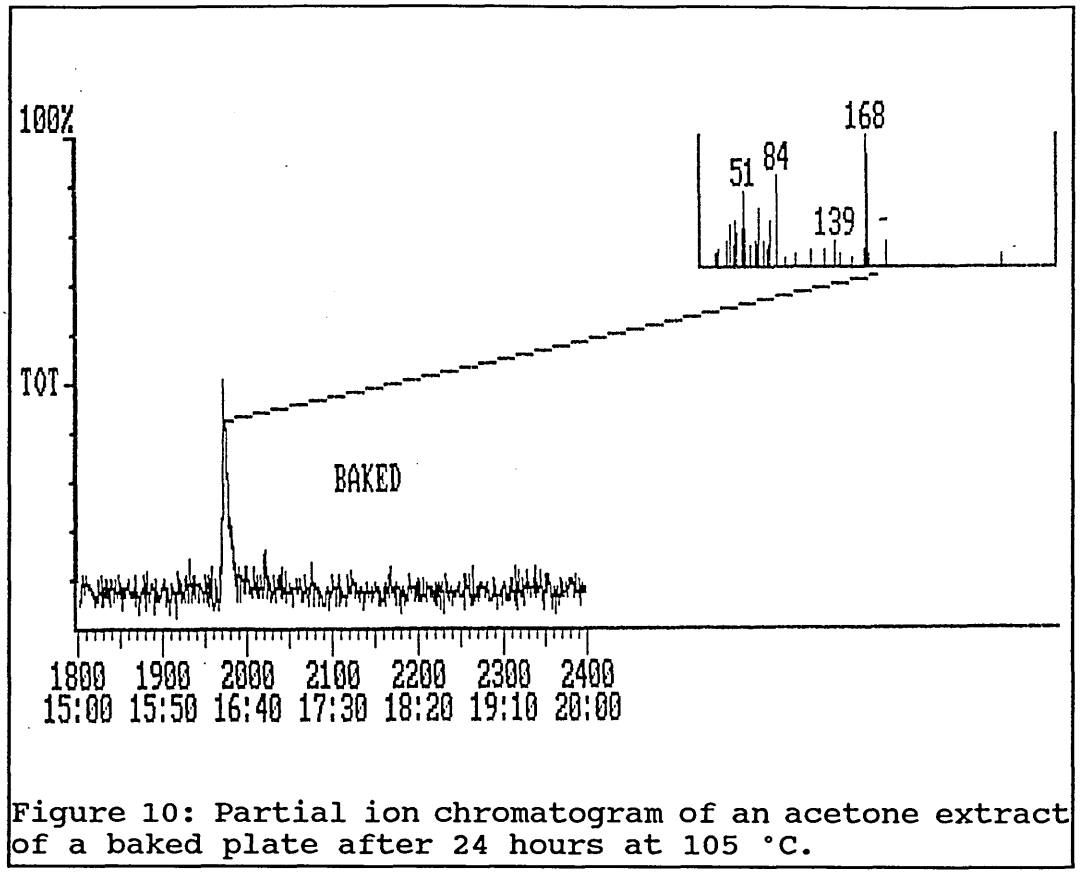


Figure 10: Partial ion chromatogram of an acetone extract of a baked plate after 24 hours at 105 °C.

It was important to run a chromatogram of an unheated plate extract because otherwise there was a danger of being misled by possible decomposition either in the heated GC injector and oven or in the mass spectrometer. The total ion current of the unheated extract shows no evidence for these effects (Figure 11).

It had been expected that the diazodiphenylamine salt would decompose in accordance with the Balz—Schiemann reaction to give 4-fluorodiphenylamine in line with scheme 10. This would have given a molecular ion at 187 Daltons. However the decomposition product spectrum shows no peak at 187, but a possible molecular ion at 169 (just after the stronger marked peak at 168). A search of the mass spectrometer computer library gave a good match for diphenylamine which has molecular weight 169. This is a very important result which shows that the Balz—Schiemann reaction is not the primary decomposition mechanism. It indicates that reaction proceeds via hydrogen abstraction from other compounds in the matrix rather than replacement

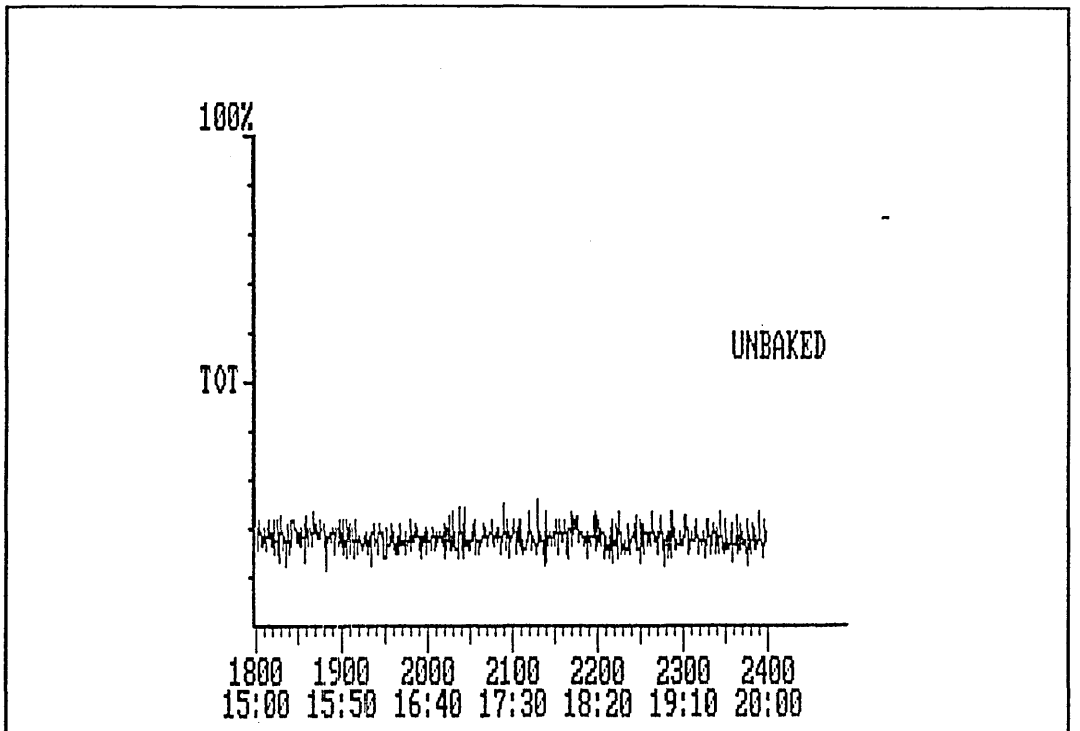


Figure 11: Partial ion chromatogram of an unbaked plate.

of the diazo group with a fluorine atom from the diazo salt counterion.

In view of the importance of this result to the development of the work contained in this thesis, an attempt was made to replicate the findings using a modification of the original instrument configuration. The major problem with the initial piece of work was working at a high noise level as is apparent from the chromatograms above. An attachment called an automatic thermal desorber was therefore used at Luton College. This is an alternative means of introducing the sample to the gas chromatograph. The desorber was linked to an identical combination of gas chromatograph and ion-trap mass spectrometer as used in the first experiments which resulted in Figures 10 and 11 above.

This time a strip of plate only about 2 mm. wide and 3 cm. long was placed in a desorber tube. The plate was heated in a controlled cycle to a preset temperature of 250 °C. All the volatiles are trapped in a cold trap at

-30 °C. After 8 minutes the trap is "fired", which is a rapid heating step to flush all the volatiles as a concentrated "slug" onto the head of the column. Thereafter the analysis is as before. The main advantage of this means of sample introduction is that all the volatiles from the piece of sample plate are flushed onto the column in one go. This gives a much greater amount of sample injected compared to the conventional approach of only injecting typically 0.5 microlitres. The other advantage is that the sample is not predissolved in a solvent. This means there are no interferences from either the comparatively massive solvent peak or any trace impurities that it may contain.

Interesting results were obtained. Figure 12 shows the relevant part of the total ion chromatogram.

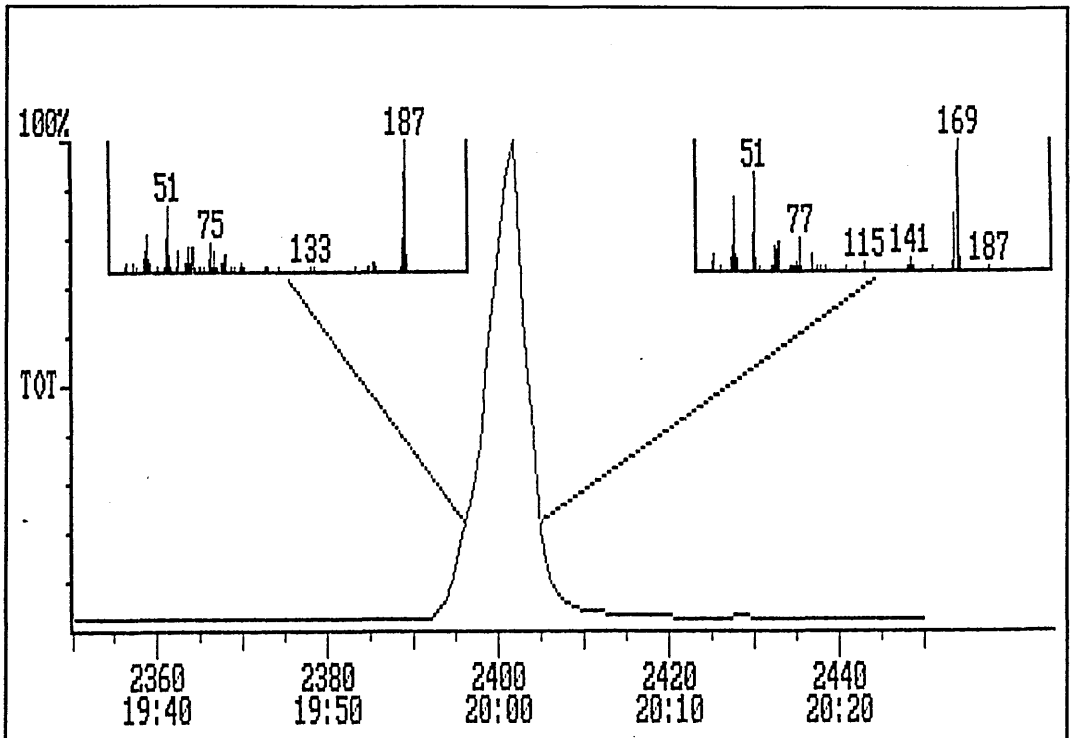


Figure 12: Thermally desorbed positive plate total ion chromatogram. Mass spectra taken at points indicated.

The single additional peak is again in evidence but with a much reduced level of background noise. This enabled mass spectra to be obtained from different points

across the peak as shown in the mass spectra superimposed on the chromatogram. This was done because it was a possibility that the fluorinated diphenylamine would co-chromatograph with diphenylamine. As can be seen from the mass spectra, this is indeed what has happened. The diphenylamine mass spectrum is produced to the right of the peak, but the small shoulder at the leading edge of the peak has a clear molecular ion at 187. This is as expected for fluorinated diphenylamine. This result seemed to be in conflict with the earlier work where no evidence for the fluorinated species was detected. Further analysis of the peak was carried out by concentrating on the two molecular ions at 169 and 187 Daltons. The results of the selective ion monitoring are shown in Figure 13.

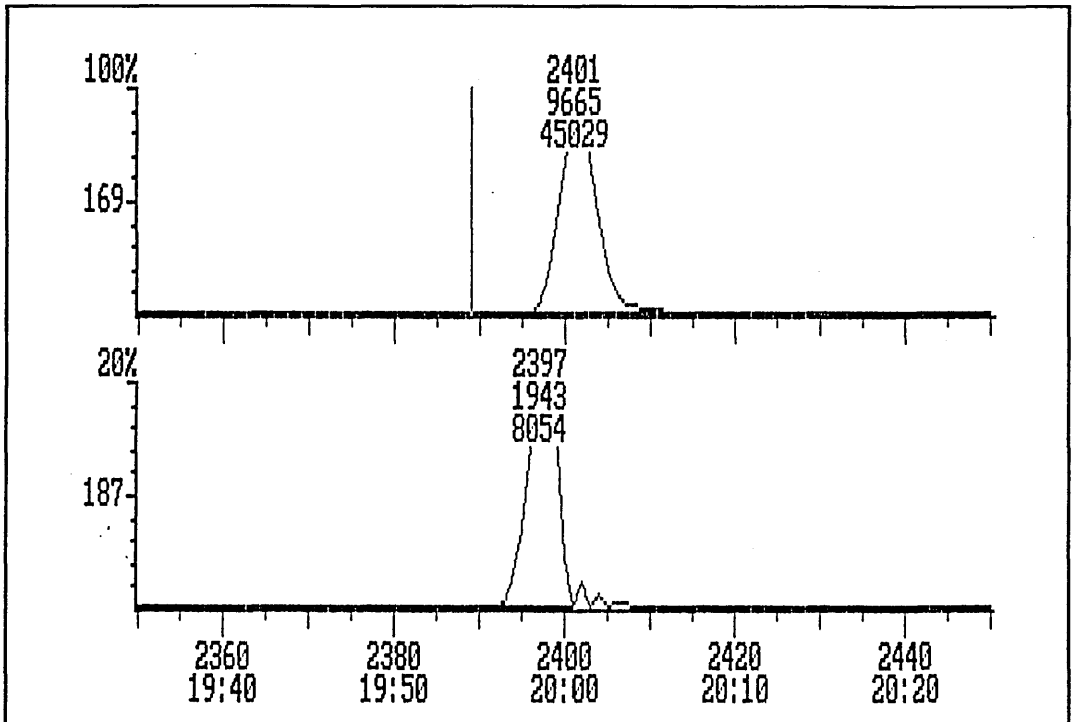


Figure 13: Selective ion monitoring at 169 and 187 Daltons of a thermally desorbed diazodiphenylamine decomposition product from a positive plate.

This shows more clearly that the fluorinated diphenylamine has a slightly shorter retention time than diphenylamine. What is more significant is that the comparative signal areas are 8054 and 45029 for the fluoro

compared to hydrogen dediazoniation reaction. Assuming the same response factor (which is a valid assumption given the similarity of the two compounds), the fluorinated diphenylamine represents only 15.2% of the total substituted diphenylamines formed. This largely explains why the presence of the fluorinated derivative was not detected on the initial analysis of the plate extract. With the higher noise level and small proportion of fluoro derivative it is not possible to detect by analysing the acetone extract. However subsequent repeat analysis has failed to show the fluorinated derivative in acetone extracts, and it may be that the thermal desorption process itself contributes to an increased amount of fluoro derivative. There is some evidence in the 187 selected ion chromatogram for low levels of other isomers of the fluoro derivative, in that there are a few small peaks with slightly longer retention times (between 20:00 and 20:05 minutes).

The conclusion of this piece of work was that the product of the thermal decomposition of diazodiphenylamine salt in a positive plate is diphenylamine with at most only a small proportion of the fluorinated diphenylamine.

2.3.3 Counter-ion decomposition products

On the strength of the well established Balz-Schiemann reaction discussed in section 1.8.1 and shown as various postulated reaction mechanisms in scheme 9 the most likely product of the thermal decomposition of diazonium salts is the corresponding aryl fluoride. In this case the complex anion loses a fluoride atom to the diazonium cation during the elimination of nitrogen. This releases the Lewis acid ie. BF_3 from BF_4^-. If the Balz-Schiemann reaction is followed it should be possible to observe a decrease in the anion concentration in line with the decrease in the concentration of the diazonium salt.

As both BF_4^- and PF_6^- are used extensively in lithography and other applications as a means of

liberating Lewis acids during photolysis reactions, diazodiphenylamine with each of these counterions was studied. The methods developed are given in detail in section 3. No literature methods for PF_6^- were found.

Measurements were carried out over a 3 week period with storage at 50 °C. Solutions in 10% cresol novolak containing either diazodiphenylamine BF_4^- or diazodiphenylamine PF_6^- were prepared, each with a diazonium salt concentration of 0.25%. Solutions were monitored for both diazonium and anion decomposition.

These experiments give some very interesting results shown graphically in Figures 14 and 15. Measurements were by ultra-violet spectroscopy, which gives a better estimate of diazonium decomposition than HPLC in simple matrices (as explained in section 2.4.4, P.114)

Firstly it is apparent that in each case the diazonium cation decomposes at a faster rate than either complex anion. This is indicative of reaction mechanisms which result in decomposition of the diazonium without involving the break up of the anion, that is to say, other than the Balz-Schiemann reaction. Reaction mechanisms are considered in section 2.3.5., P.106.

Secondly the diazonium salt with a hexafluorophosphate counterion is more unstable than the corresponding tetrafluoroborate diazonium. This is in line with the results of other work, for example by Schlesinger[66]. This paper also postulated that diazonium salts with an amino substituent (such as is the case with diazodiphenylamine, although this was not one of the compounds under consideration) did not liberate the Lewis acid readily because of the formation of a complex between the basic amino nitrogen and the Lewis acid (Scheme 21 below).

An extra heating step was required in cationic polymerisations based on initiation by Lewis acids liberated from diazonium salts depending on whether the parent salt contained an amino substituent or not. Such

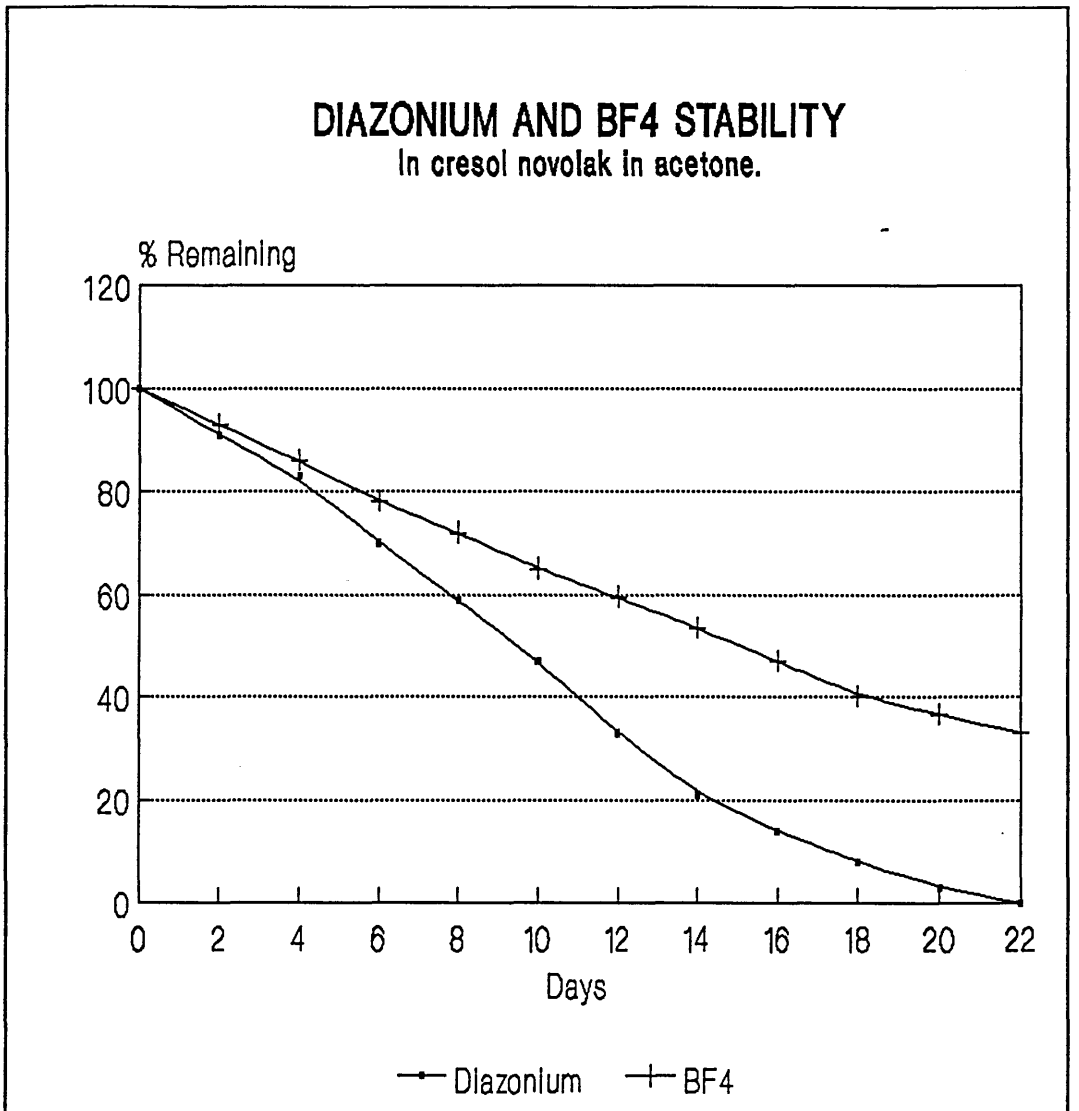


Figure 14: Comparative decompositions of diazonium and tetrafluoroborate in 10 % cresol solution.

complexes would be expected to be stronger with tetrafluoroborate compared to hexafluorophosphate as mentioned below[67]. The reduction in availability of the Lewis acid would reduce the rate of heterolytic decomposition and proportion of Schiemann decomposition products.

Experiments in non-polar solvents have shown[68] that arenediazonium salts with PF_6^- counterions couple with N,N-dimethylaniline approximately four times faster than

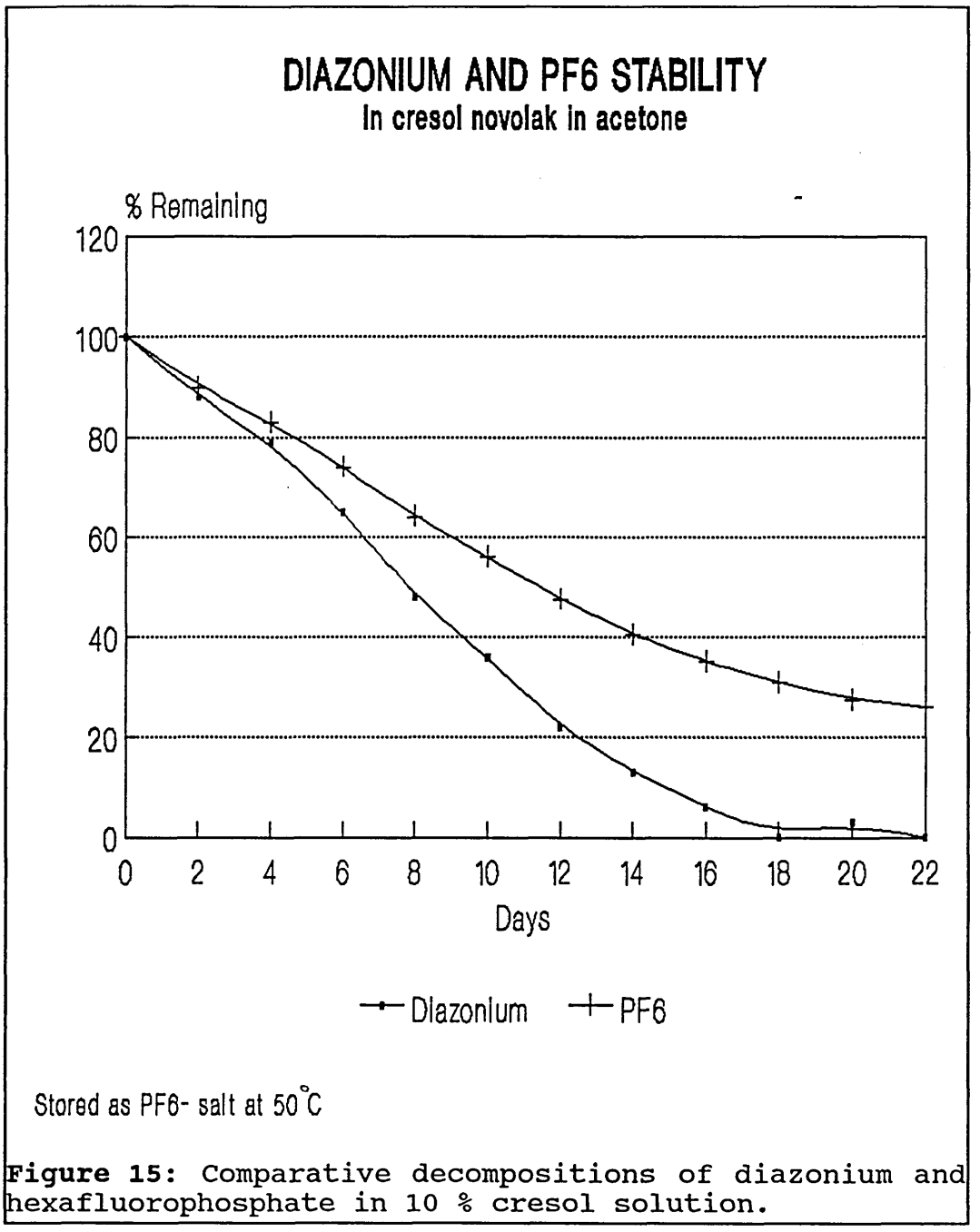
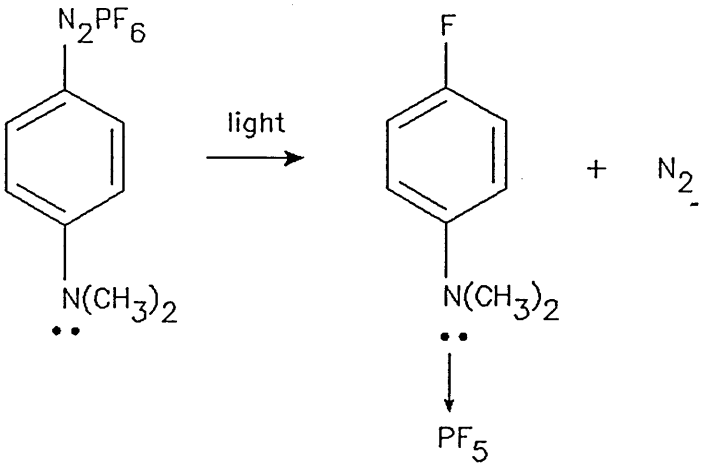


Figure 15: Comparative decompositions of diazonium and hexafluorophosphate in 10 % cresol solution.

with salts possessing a BF_4^- counterion. This is indicative of decreased electrophilicity of the cation in BF_4^- salts which indicates corresponding increased ion pairing[69].

Apart from the faster decomposition of the diazonium cation compared to the complex anion and the greater decomposition rate of the hexafluorophosphate diazonium salt, the third conclusion from this piece of work was that the hexafluorophosphate anion decomposes more rapidly



(Scheme 21: Complex formation between Lewis acid and aromatic amine)

than the tetrafluoroborate. This is as expected as the complex of PF_5 with F^- as it is observed in the PF_6^- ion is a less stable complex than the corresponding complex of BF_3 and F^-. This also applies to complexes with organic compounds such as amines, ethers and other bases[67]. This results in the strength of the P-F bond being considerably less than that of the B-F bond[70]. A statistical factor would also favour removal of a fluoride ion from hexafluorophosphate over that from tetrafluoroborate.

The two increases in decomposition observed, of both the cation and anion in hexafluorophosphate salts, are clearly linked in that factors that favour decomposition of one ion will also tend to favour that of the other. A common mechanism is invoked.

However literature results of analysis of product proportions show a higher yield of fluorodediazoniations from the tetrafluoroborate than the hexafluorophosphate[67]. These surprising results indicate that for thermolysis in organic solvents of low polarity, diazonium cation-anion pairs as well as free diazonium cations are kinetically active diazonium ion species.

Further insight can be obtained on the two salts by infra-red analysis. Earlier work indicated that for diazonium salts in general the tetrafluoroborate was ionically bonded to the diazonium ion, but salts of less

strong Lewis acids had some covalent character [27]. However it was further stated that these differences were less pronounced when amino substituents resulted in some transfer of the positive charge. In the latter cases the N-N frequency did not depend on the anion and they concluded that with the charge transfer the interaction between the N-N group and the complex anions has been reduced.

The effects of the other anion counterions on the rate of diazonium decomposition will be discussed in greater detail in section 2.5.2.

2.3.4 Detection of oligomeric products

In section 2.3.2 it was reported that during the analysis of plate extracts, the main decomposition product detected was diphenylamine with an unexpectedly small amount of the fluorodiphenylamine. Methods were developed by both HPLC and GC for the measurement of the diphenylamine component. These methods did not differentiate between the fluoro and hydro dediazoniation products but gave a total of these simple products. The results indicated that in both cresol and cresol novolak solutions between 50 and 60 % of the diazodiphenylamine decomposition gave fluoro or hydro dediazoniation products.

What had happened to the rest? Diazo compounds are well known for undergoing coupling reactions, usually in the presence of base. This would give rise to higher molecular weight species that would contain the azo group, as in azo dyes. As these would be difficult to detect either in the presence of cresol novolak (due to its spread of molecular weight) or with other monomeric coating components present, a simple solution of diazodiphenylamine in 10 %w/v m-cresol solution was studied. This was allowed to decompose at 40 °C for 20 days. At the end of that period the diazonium salt had decomposed by 42 %. From the analysis of the decomposed

solution, 58 % of this decomposition could be accounted for by the formation of diphenylamine and fluoro diphenylamine. Earlier work reported in this account indicates that the vast majority is present as diphenylamine, not the fluoro substituted product. A further 5 % was detected as hydroxy substituted diphenylamine (probably due to reaction with the small amount of water present as a contaminant).

The solution was analysed by gel permeation chromatography, which gave the chromatogram shown below. This analysis was carried out using a 500 Å column that is of sufficiently low pore size to give separation of low

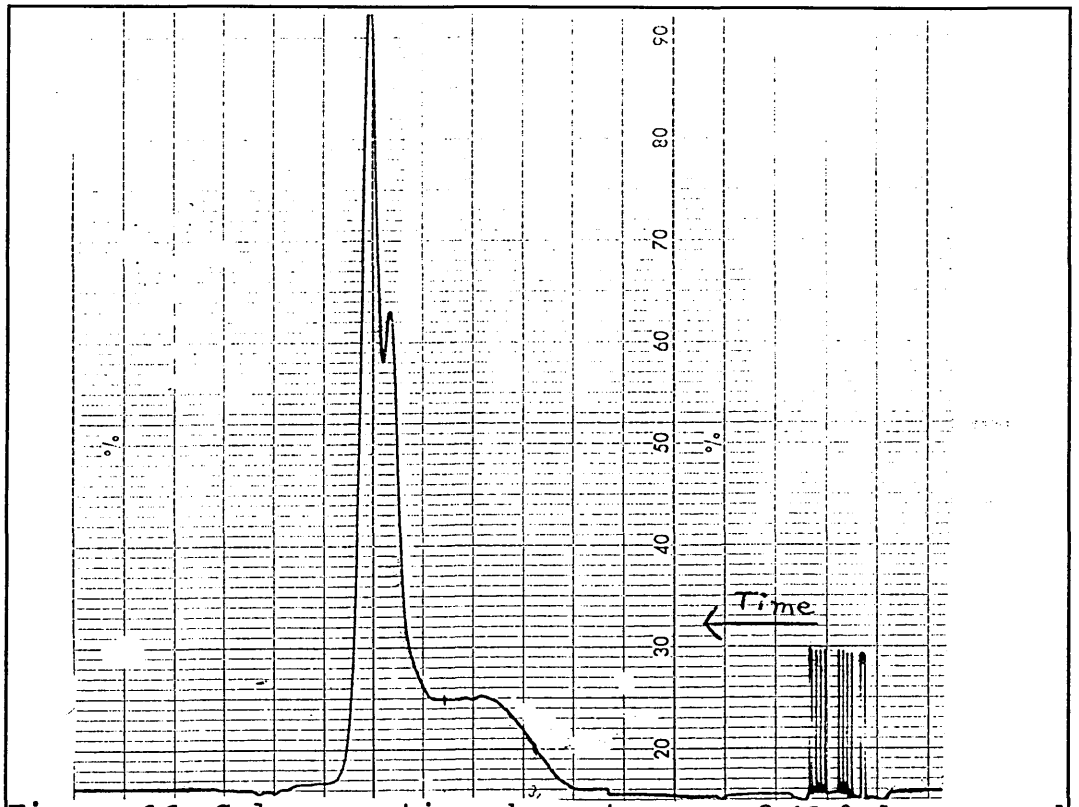


Figure 16: Gel permeation chromatogram of 42 % decomposed diazodiphenylamine in 10 % w/v m-cresol.

molecular weight species. The chromatogram shows two merged low molecular weight peaks that can be assigned to the m-cresol and acetone in the decomposition solution. Diazonium salts are fully retained by this column system. However the important point to note is the broad peak on the higher molecular weight end of the chromatogram (towards the injection code markers). This is presumably

due to coupled species and was not present in a chromatogram of the fresh solution. A polystyrene calibration indicated that the molecular weight average of the broad band was at 1500 Daltons.

The solution was further analysed by mass - spectroscopy. This was done because the components of higher molecular mass should be detectable in the matrix of low molecular weight species. A fraction was taken from the GPC separated broad band and analysed by mass spectroscopy at York University. This gave the spectrum shown below.

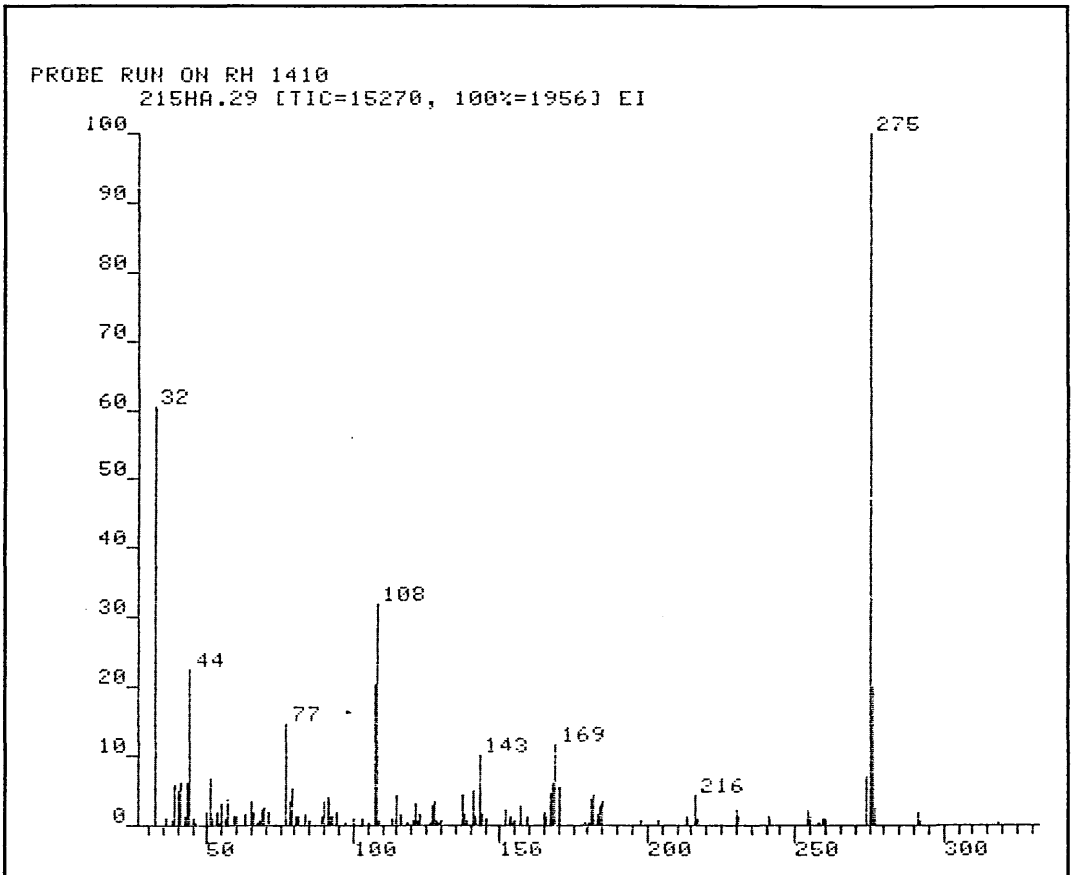
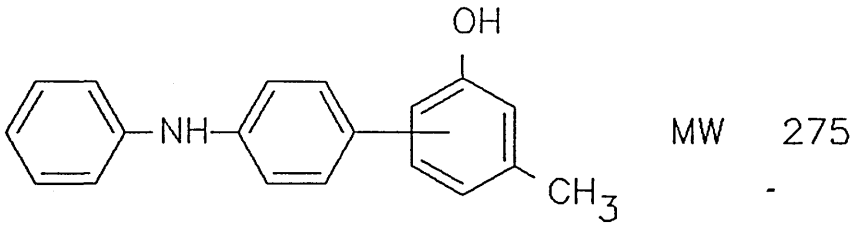


Figure 17: Mass spectrum of the high molecular weight fraction from a diazodiphenylamine decomposition.

The spectrum has its strongest peak at a mass of 275. This would correspond to the product of the reaction of the diphenylamine residue with the cresol.

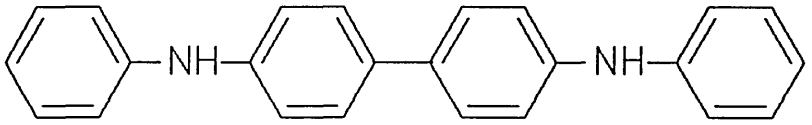
The other peaks of interest are at masses 169 for diphenylamine and at 108 for cresol. These are probably



(19: Diphenylamine/m-cresol product)

due to a combination of overlap of the GPC fraction with the monomeric components of the sample, and to fragmentation of the molecular ion at 275. To eliminate the possibility that the product of mass 275 could have been formed on the mass spectrometer probe, a blank was carried out using some fresh stability solution which gave no peaks at higher masses.

Further evidence for the structure of the higher molecular weight species came from the mass spectrum of another GPC fraction which gives a molecular ion at 336 Daltons. This can be interpreted as two diphenylamine units linked together to give diphenylbenzidine and isomeric products (depending on the position of substitution).



MW 336

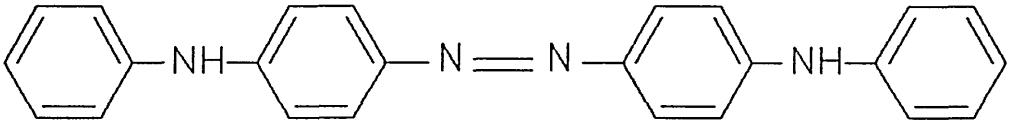
(20: Diphenyl benzidine)

Diphenylbenzidine is available commercially from Aldrich Chemicals. A sample of this was used to develop an HPLC analysis method and the amount present in the decomposition solution was measured. This gave a value that can be expressed as a percentage of the diazonium salt lost that has formed this product. The full results are express in the Table 14 below.

Related work looking for decomposition products formed on decomposition of diazodiphenylamine salts in

solvent only, indicated the formation of small amounts of higher molecular weight products in this matrix as well.

Analysis of these products by mass spectrometry gave a molecular ion at 364. In the absence of other compounds in the matrix, the diazodiphenylamine is more likely to undergo self coupling reactions and this is what is observed. The 364 molecule can be assigned to the following structure (21).



MW 364

(21: Coupled diazodiphenylamine products)

Further evidence for the presence of decomposition products retained some diazonium character, comes from the difference in decomposition rates as measured by HPLC compared to UV/visible spectroscopy. HPLC shows large losses of the diazonium salt analyte but UV/visible spectroscopy indicates a lower loss of total diazonium groups. This is described in detail in section 2.4.

A summary of the decomposition products identified in this section is given in the table below.

Table 14: Percentages of decomposition products formed during diazodiphenylamine salt decomposition in m-cresol solution.

Decomposition Product	% (Approx.)
Diphenylamine	50
Fluorodiphenylamine	8
Hydroxydiphenylamine	5
Diphenylbenzidine isomers	3
Diphenylamine/m-cresol (structure 19)	34
Other oligomeric species (eg structure 21)	

This identification and quantification, where possible, of the decomposition products is the main evidence for identifying the underlying decomposition mechanism that is operating. Knowing the mechanism of decomposition is a significant aid in designing further measures to limit the diazodiphenylamine decomposition rate.

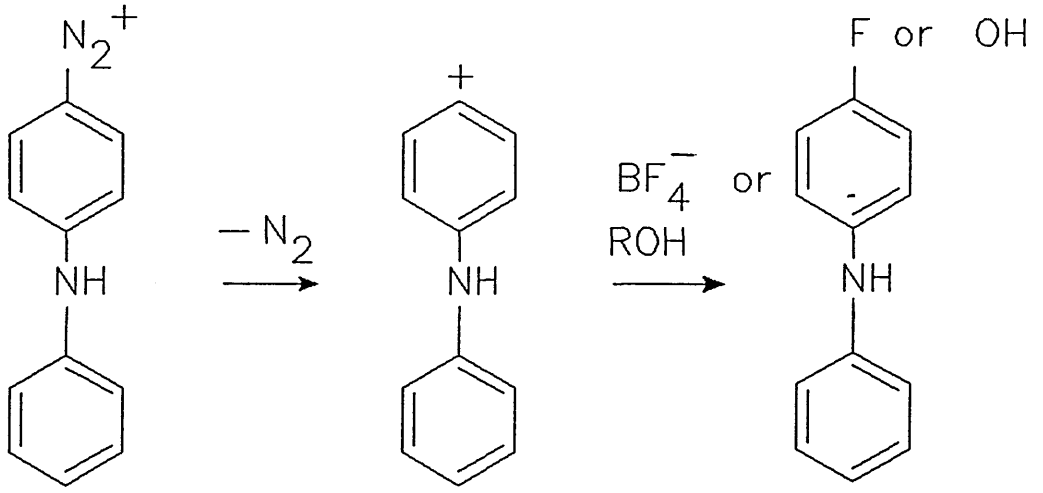
2.3.5 Decomposition Mechanism

The possible decomposition mechanisms were discussed in an earlier section (1.8.3). In scheme 12 (P. 40) the results of cationic and radical decomposition are shown. These two extremes arise either from internal electron transfer to the C-N bond, resulting in heterolytic fission and a cationic mechanism; or via external donation of an electron resulting in homolytic fission of the ring-diazo bond and a radical mechanism. The cationic mechanism proceeds, as the name implies, via the formation of a positively charged cationic intermediate. In the presence of water or in solvents such as methanol, the cation can react to form hydroxy or methoxy substituted products. This is also the mechanism followed in the Balz-Schiemann reaction, whereby fluoro-dediazoniation occurs. Abstraction of positively charged hydrogen is not possible in this mechanism.

Examination of the list of products of diazodiphenylamine decomposition, and their proportions, in the above table shows that the cationic mechanism is only in evidence from the formation of a relatively small amounts of the fluoro and hydroxy substituted products. Their formation proceeds as in the scheme below.

The generation of diphenylamine as the major decomposition product, and the formation of higher molecular weight oligomers, is characteristic of a radical decomposition mechanism.

The formation of products with an azo link such as structure 21 is consistent with either electrophilic



(Scheme 22: Cationic mechanism for diazonium decomposition)

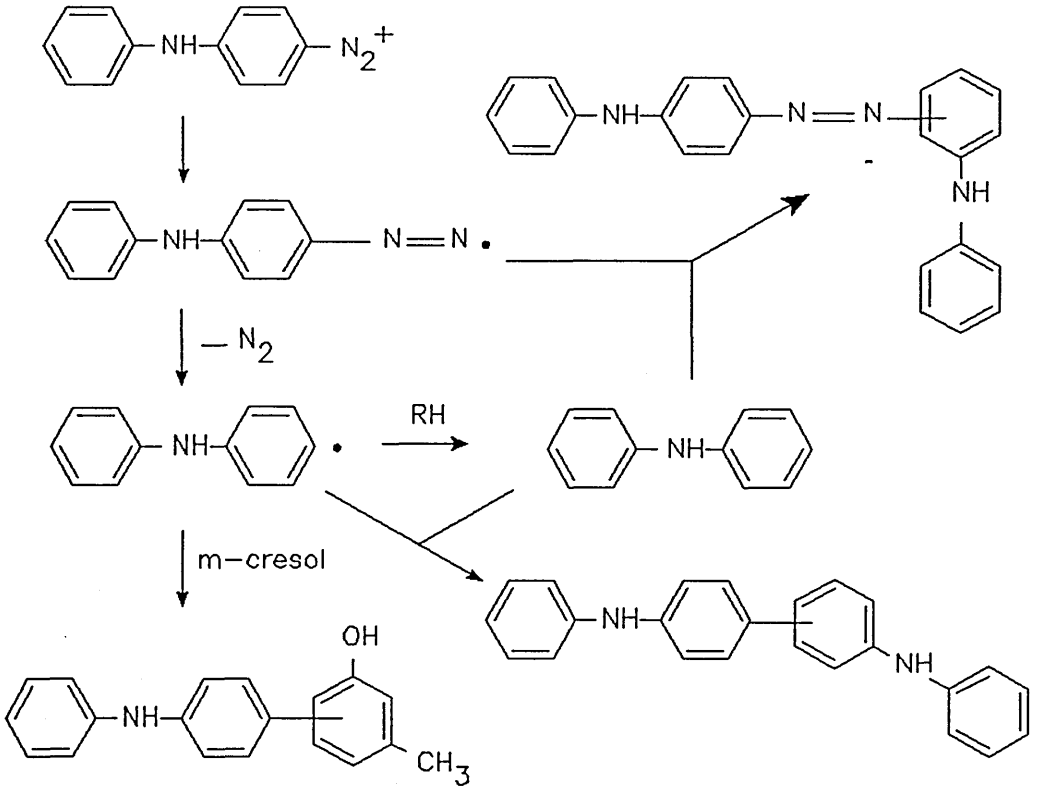
substitution or with the formation of a radical intermediate that can either react with other species present in a chain reaction, or lose nitrogen to give a second radical. These further products are evidence of the predominating radical mechanism. The second radical can either be terminated by hydrogen abstraction from other components in the matrix, to give diphenylamine, or can react further to give substituted products of cresol (structure 19) and polydiphenylamine oligomers (structure 20). This is summarised in scheme 23 below.

The most likely source of hydrogen that could be abstracted is from the solvent, as this is the component at highest concentration in the matrix. There was some evidence for this in the formation of diacetone alcohol which was detected at low concentrations by GC/MS.

$CH_3CO.CH_2C(CH_3)_2OH$

(22: Diacetone alcohol)

One effect of the radical mechanism is that it will give rise to a wide range of alternative products depending on the nature and concentrations of other components of the matrix. Radical reactions, such as the substitution of the diphenylamine radical in m-cresol, are not directed by the electronic status of the target



(Scheme 23: Radical reaction mechanism for diazonium decomposition)

aromatic ring. This gives products in a range of substitution positions. Whether chains of diphenylamine molecules or terminated diphenylamine will predominate will depend on the ease of hydrogen abstraction and the relative concentrations of diazodiphenylamine, diphenylamine and the other matrix components. If m-cresol is absent, diphenylamine and the azo-diphenylamine (structure 21) will predominate giving the polymeric products observed under these conditions.

The overwhelming evidence for a largely radical as opposed to cationic mechanism gives rise to some further possibilities for stabilising the system. These will be described in a later section, but include using radical traps and studying the effects of oxygen on the system.

Whether a radical or cationic mechanism predominates depends on the ease of transfer of an electron to the diazo-carbon bond. If this can readily be accomplished by

internal transfer, the cationic mechanism will be more common. For diazodiphenylamine it has been shown that this is not the case. Electron transfer is more readily accomplished from the matrix, giving rise to the homolytic radical mechanism. Other diazonium salts may undergo decomposition via the cationic mechanism and may be inherently more stable. In order to study the decomposition of alternative diazonium salts, it is important to assess the various methods of analysis available so as to select the most appropriate for the matrix and for the information required from the data.

2.4 METHODS OF ANALYSIS OF AROMATIC DIAZONIUM SALTS

During this investigation into the stabilisation of diazonium salts in lithographic systems, several very different techniques were utilised to quantify the aromatic diazonium compounds themselves. In the literature there also a range of methods described, but only a portion of these are applicable to the matrices encountered in lithographic coating solutions, plates and stability solutions.

Many of the earlier methods of analysis are only of use for diazo compounds in isolation and are not specific enough particularly in the presence of other diazo compounds.

2.4.1 Chemical Methods

Until the development of instrumental methods of analysis, the most commonly used methods were those based on reductometric titrations, coupling reactions and gasometric reactions.

Reductometric Titrations

These reactions must be carried out in the absence of oxygen. The most widely used method of this type is titration with $TiCl_3$. This can be carried out on a micro scale by adding an excess of the $TiCl_3$ solution to an

acetate-buffered solution of the sample at room temperature, and back-titrating the excess $TiCl_3$ with a ferric alum solution, using ammonium thiocyanate as an indicator[71].

$$2PhN_2^+Cl^- + 4TiCl_3 + 2HCl \rightarrow PhN{=}NNPhNH_2 + 4TiCl_4$$

(Scheme 24: Titrimetric assay of diazonium salt)

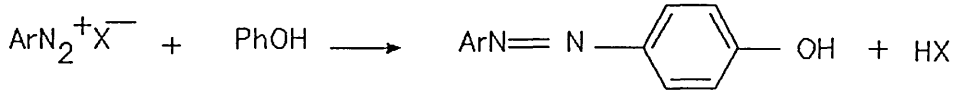
However the method is also applicable to azo groups and if these are formed or are present from other components (such as dyes) in the matrix, they will interfere with the diazonium determination.

Chromous chloride has been used in a similar reaction in a weakly acidic solution. The excess $CrCl_2$ is measured potentiometrically with a ferric alum solution[72].

This method is fast as well as quantitative, but will suffer from the same problems as for titanous chloride, in that any other compounds present capable of reduction will interfere. Other reductometric titration methods based on vanadium (II) sulphate, sodium hyposulphite and hydroiodic acid have also been described. These predate the development of instrumental methods of analysis and are insufficiently selective for all but the simplest of matrices.

Coupling Methods

The high reactivity of aromatic diazonium compounds can be used to develop specific analytical methods for their determination. In particular coupling with aromatic amines or phenols to yield azo dyes.



(Scheme 25: Coupling reaction for diazonium determination)

The method is very selective as few other compounds couple with these reagents. For determinations on samples of diazonium compounds in simple matrices, an excess of coupling agent is added and coupling carried out in acidic solution. The excess coupler can then be measured by

titration with standard benzene diazonium chloride solution using an external indicator. This method has its problems caused by the slow rate of coupling and the difficulty in observing the endpoint[73].

Coupling reactions have found use in this investigation when used in conjunction with HPLC. In a complex matrix with several strongly absorbing species present, the addition of coupling reagents can have two useful effects. After coupling the diazonium absorption will be lost and replaced by that of the azo group which is usually at longer wavelengths where there will be fewer interferences. Secondly, the diazonium group is ionic, and can give rise to either broad peaks in HPLC or adsorption effects in gel permeation chromatography. Both these are eliminated after the formation of the azo link. The coupling reactions used were as an extension of the chromatographic methods and no quantitative measurements were made based on coupling methods alone.

Gasometric Methods

Solutions of aromatic diazonium salts readily decompose on heating with mineral acids to give phenols and nitrogen. When heated with acid and cuprous chloride, chlorobenzenes and nitrogen are obtained. Nitrogen is quantitatively liberated and determined volumetrically in a nitrometer. The method is very selective since few compounds liberate a gas under the above conditions. The general procedure has been described in detail[74]. A high degree of accuracy and precision is claimed, particularly in the case of the cuprous chloride reaction. The reproducibility is claimed to be +/- 0.3 % and the maximum error +/- 1.0 %[75] . However, the procedure is tedious and time consuming. The methods are inaccurate if organic degradation products containing nitrogen are formed, if atmospheric oxygen is absorbed during decomposition or partial coupling with decomposition products occurs. My own experience with gasometric methods is that even when used for tests on relatively pure diazonium raw materials, a high degree of practice is

required to get reproducible results. Furthermore the methods are not appropriate for rapid throughput of results or for widely varying matrices and concentrations of diazonium species. For these reasons gasometric methods were not used in this investigation.

2.4.2 Polarographic Methods

Arene diazonium salts are reduced at a dropping mercury electrode. Two half-waves have been observed and tabulated, but their positions have only qualitative significance since the shapes of the waves are irregular. It has been suggested[76] that the product of reduction of arenediazonium salts is an aryl hydrazine.

$$ArN_2^+ + 4e^- + 3H^+ \longrightarrow ArNHNH_2$$

(Scheme 26: Reduction reaction of arenediazonium salts)

In spite of the fact that the waves are complex, their heights vary directly with concentration. The diffusion current is compared with a calibration curve of current against concentration. Alternatively, methods have been developed based on the first half-wave of the aromatic diazonium group occurring at a potential significantly below that of the azo group. This has been used in the determination of diazonium salts by a coupling titration in an amperometric titration cell equipped with a dropping mercury electrode. A known aliquot of 1-phenyl-3-methylpyrazolone in the cell is titrated with the diazonium salt solution. As long as coupling occurs no reduction of the diazonium salt takes place and no current flows. As soon as the pyrazolone has been consumed, the end of the titration is indicated by a current flow which is directly proportional to the concentration of excess added diazonium salt[77].

Although polarographic methods were used to compare the relative reduction properties of diazonium salts in this investigation, the quantification of diazonium salts was carried out by chromatographic and spectroscopic

techniques. This was due to the difficulty of applying the polarographic technique to the complex matrices that constituted the majority of the sample tests in this study.

2.4.3 Chromatographic Methods

Before the extensive development of HPLC, gas chromatography was used to determine aromatic diazonium salts indirectly. Samples were pyrolysed at 160 °C and the nitrogen from the pyrolysis eluted on a column of a molecular sieve 5A and determined quantitatively by comparison of the nitrogen peak areas with calibration curves of injected nitrogen samples[78]. This can be regarded as an extension of the gasometric methods mentioned above, with more quantitative recovery and detection of the evolved nitrogen.

The advent of High Performance Liquid Chromatography (HPLC) has brought perhaps the most powerful analytical technique of those considered so far. This is analogous to gas liquid chromatography but is more widely applicable, in that it may be used for non-volatile organic compounds. It can be used for direct diazonium salt determination. Detection is usually by ultra-violet/visible spectroscopy. Diazonium salts absorb strongly in the UV region or in many cases, even in the visible. The problem with the HPLC of diazonium salts lies in their ionic nature. Simple mixtures of solvent and water, as used for reverse phase chromatography, give rise to poor peak shape. This can be improved so as to give an acceptable peak, suitable for quantification purposes, by the use of an acid buffer and the addition of lauryl sulphonate as an ion pair reagent.

The advantage of HPLC over <u>all</u> the other methods is its specificity. Plate extracts and diluted coatings can be analysed even though they contain dye mixtures, novolak resin or other diazo compounds. By selecting an appropriate detector analysis wavelength or choosing a different blend of mobile phase eluents and eluent buffer

salts, the separation of the diazonium salt from the rest of the matrix components can be optimised. Analysis time is rapid, usually about 10 minutes after injection. There is also the possibility, for example, of being able to assess the build up of decomposition products during decomposition experiments.

For these advantages, HPLC was widely used particularly in the initial parts of this investigation. However it does have two disadvantages. Firstly, although much faster than many other methods, the equipment does take about an hour to set up, and the complexity of the eluent means it may need minor adjustment that requires a further time to re-equilibrate. For simple systems, without interfering species, some of the spectroscopic techniques described below are more appropriate. Secondly, although very specific, this in itself can be misleading. During decomposition experiments, frequent mention is made of loss of the diazonium group as decomposition proceeds. This is quite correct as it is the diazonium group that is the unstable entity. As was shown in an earlier section, decomposition can proceed such that the decomposition mechanism can involve a second diazonium salt molecule. In its simplest form if half the diazonium salt present lost its diazo function and the residue coupled with the other half, the HPLC analysis would show all the diazonium salt had disappeared. Although this would be correct, in that all the diazonium salt had now become a coupled species, it would be misleading because half the diazo groups would be still intact. HPLC should, therefore, be used in combination with methods that give a direct indication of the diazo group loss. Some of the best of these methods are spectroscopic ones.

2.4.4 Spectroscopic Methods

UV/Visible Spectroscopy

Literature shows that aromatic diazonium salts in 0.1 M HCl display maxima in the 220-300 nm region which are

strongly dependent on ring substituents and their position. The unsubstituted benzenediazonium chloride absorbs at 262 nm. Benzene diazonium fluoroborate in acetonitrile absorbs strongly at 261 and 296 nm. Its spectrum and that of several mono and polymethoxy derivatives have been recorded in the 200-450 nm region and assignments of electronic transitions were made by means of molecular orbital theory[79]. The electronic spectra of para and meta-substituted benzenediazonium fluoroborates have been recorded and tabulated. The para series had a single band in the range of 260-380 nm, and the meta series has two bands around 270 nm and in the range 300-350 nm. As indicated before, the maxima are strongly dependent on substituents and their positions.

Substituted p-aminoaryl diazonium salts have been assigned a quinoid structure (11) which gives rise to strong absorption at longer wavelengths in the region 350-400 nm. The diazodiphenylamine salt is in this category and gives a maximum absorbance (λ max) of 378 nm as shown in Figure 3 (P. 64). However what is also apparent from Figure 3 is that other coating components, in this case a diazo ester, may also absorb in the same part of the UV/visible spectrum. These include some of the dye absorptions as well as the diazo ester. If these other components are present, UV/visible spectroscopy is not the preferred analytical technique, particularly as the diazonium salt is a relatively minor component of the coatings. However UV/visible spectroscopy is a very rapid technique. Once the solution is diluted to the correct strength and the instrument is set to the λ max. or other appropriate wavelength, it only takes a few minutes to take a measurement. Although interference from some coating components is a limitation of the technique, there is no interference from the major coating component- the cresol novolak. As the diazonium salts under consideration absorb in the 350-400 nm region, there is also no interference from coating solvents such as acetone which has a "cut-off" of UV absorptions below 320 nm.

The simplicity and rapidity of the technique resulted in it being widely used for stability trials of solutions of diazonium salts in solvent alone or in the presence of alkylhydroxybenzenes or cresol novolak. It was particularly useful when a range of alternative-diazonium salts were investigated, in that method development is much simpler by UV/visible spectroscopy than HPLC. Initially use of UV/visible spectroscopy was restricted because of possible misleading results from absorption in the same region as the diazo by the decomposition products. Subsequent identification and quantification of the decomposition products showed this concern to be unfounded.

In section 2.4.3 it was explained that HPLC can show a large amount of diazonium salt decomposition which might be misleading if the salt was coupling with itself. This is because only one of the diazo groups might be lost when two molecules coupled. This was investigated by carrying out a decomposition trial in 10% w/v cresol novolak solution, analysing the decomposition of the diazonium salt by both HPLC and UV/visible spectroscopy. The results are shown in the table below.

Table 15: Comparison between HPLC and UV/vis measurement of diazonium salt percentage decomposition.

Days at 40 °C	HPLC (loss of diazonium salt)	UV/vis (loss of chromophore)
2	11	9
4	15	13
8	30	25
12	38	33
16	45	37

Though both techniques show the same gradual loss of the diazodiphenylamine salt, the HPLC method gives consistently higher losses. This is useful evidence for the coupling reaction already described. Furthermore, it shows that care must be taken in any comparative

experiments to ensure that the same method of analysis is used.

Infra-red Spectroscopy

No discussion of specific techniques targeted at diazo group decomposition would be complete without mention of infra-red spectroscopy. Aromatic diazonium salts exhibit the NN stretching frequency at around 2260 +/- 20 cm^{-1}, occasionally in the range 2295-2110[26]. Diazodiphenylamine is in the latter category and has its strongest absorption in this region at 2177 cm^{-1}.

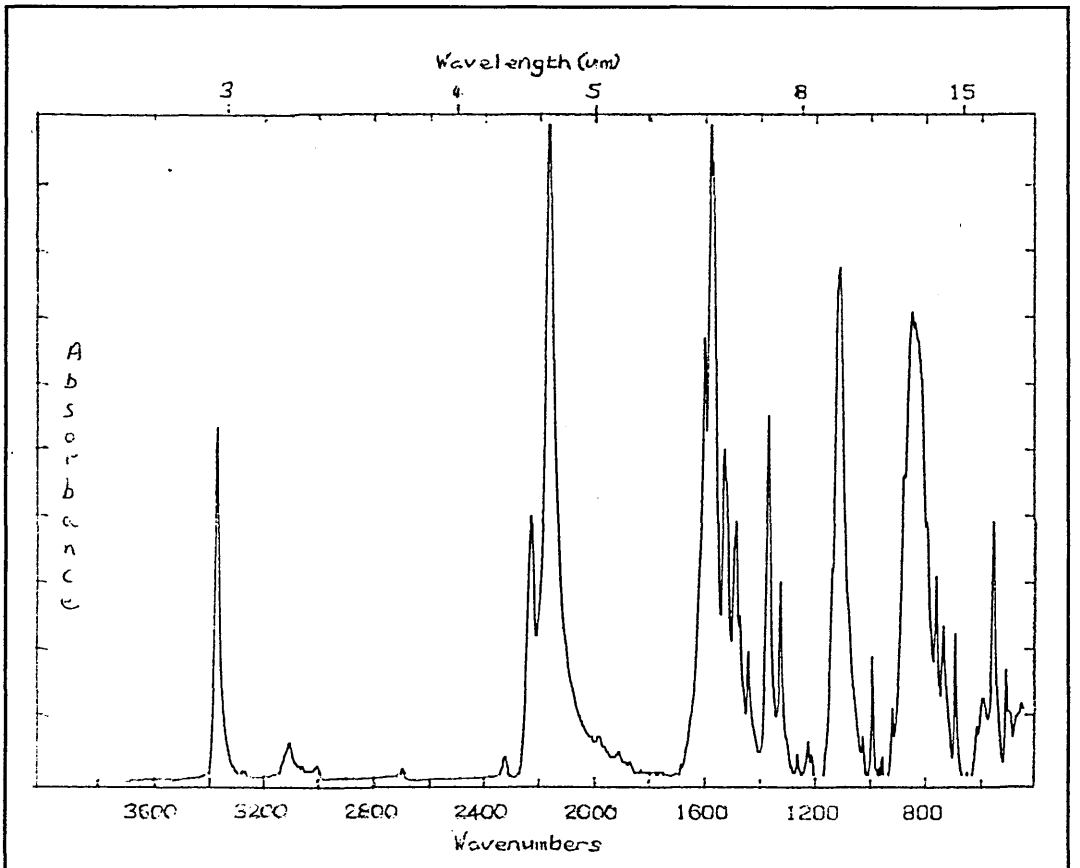


Figure 18: Infra-red spectrum of diazodiphenylamine hexafluorophosphate (KBr disc)

Although there are other absorptions in the spectrum, that in the 2200 cm^{-1} region would be expected to be directly related to loss of diazo character. It is also fortunate that this region is relatively free from many other absorptions that can make quantitative infra-red difficult in the presence of other species. It was hoped

that this technique would be applicable to coating solutions and plate extracts.

A series of solutions were prepared containing diazodiphenylamine hexafluorophosphate at varying concentrations around those encountered in coatings and solution stability trials. The solutions were in 10 %w/v m-cresol solution in acetone. A variable path length liquid cell was used with a Fourier Transform Infra-red spectrophotometer (FTIR).

Results were disappointing. Although FTIR is more sensitive than dispersive instruments, it is still much less sensitive than UV/visible spectrometry, particularly for species such as the diazo group which exhibits a strong UV/vis. absorption.

The test solutions were scanned 100 times, and analysed as undiluted solutions. Improved spectra were obtained by subtracting a blank solution spectrum of the m-cresol in acetone. The level found in coating solutions is as in the figure below (figure 19).

The rather poor spectrum after the subtraction has an absorption of only 0.04 for the diazo band. The other absorptions are from the other groups that comprise the diazodiphenylamine and its counter-ion. Given the level of noise in the spectrum, and the fact that this is the maximum initial level for comparing decomposition tests with, it was not feasible to continue with infra-red for quantitative analysis.

2.4.5 Analysis techniques conclusion

From the above discussion, two techniques emerge as being of widest applicability for quantitative diazonium measurement in the presence of other plate and coating components. These are HPLC and UV/visible spectroscopy. HPLC can be thought of as an extension of the use of UV/visible spectroscopy, in that it incorporates UV/visible spectroscopy as the detector. In simple matrices of diazonium compound and solvent, or diazonium

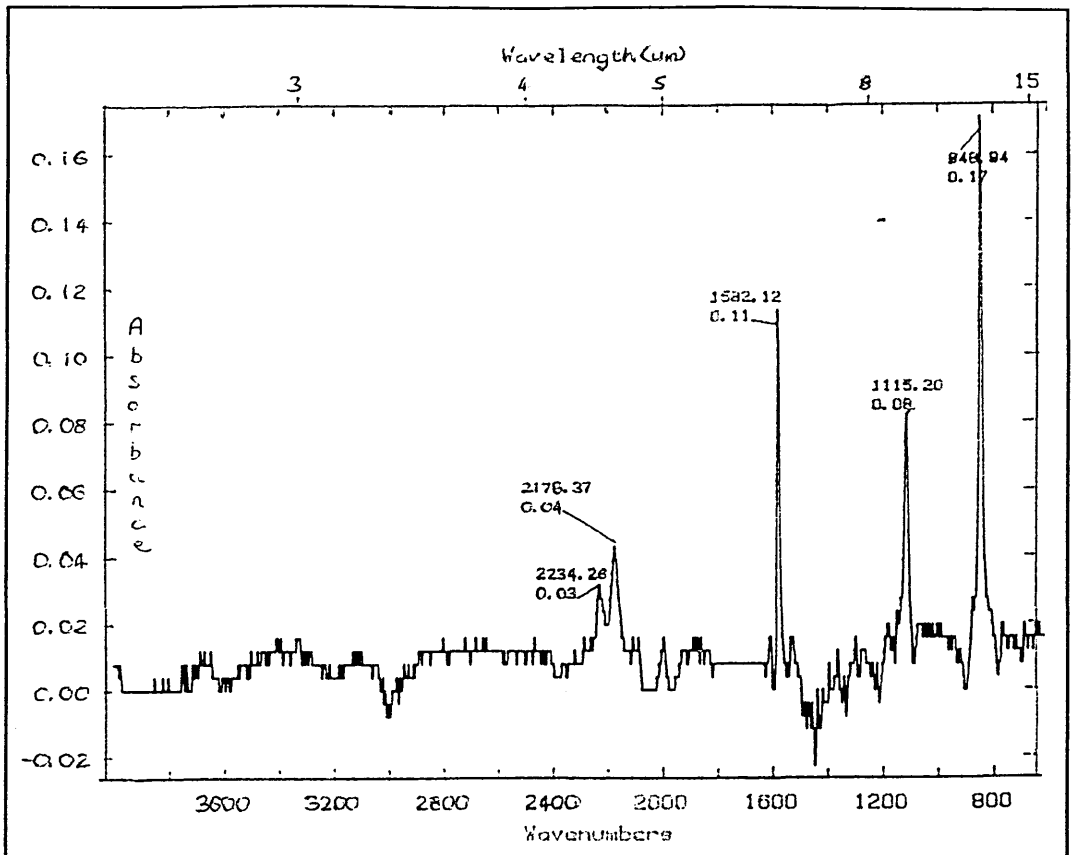


Figure 19: Infra-red spectrum of diazodiphenylamine hexafluorophosphate in 10 % m-cresol in acetone after subtraction of the cresol solution spectrum.

compound, solvent and phenolic species, UV/visible spectroscopy was the method of choice. When other compounds that absorb in the same part of the UV/visible spectrum were in the matrix, HPLC had to be used. This would encompass solutions containing diazo ester or dyes.

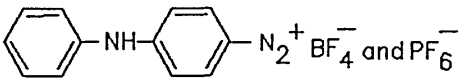
Whichever technique was used, comparisons between solution stabilities were always carried out using the same method of analysis. This was because HPLC measures the concentration of the diazonium compound under investigation, whereas UV/visible spectroscopy will include any decomposition products that retain the diazonium functional group.

2.5 ALTERNATIVE DIAZONIUM SALTS AND COUNTERIONS

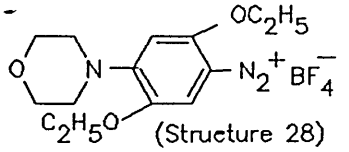
Thus far this investigation has been concerned with diazodiphenylamine with either a tetrafluoroborate or hexafluorophosphate counterion. This was because they are widely used as acid release agents and serve as good models for the study of diazodiphenylamine/formaldehyde polymers used in negative working plates. However it was important to identify whether other commercially available diazonium salts were significantly more or less stable as this might provide further insight into the decomposition mechanism. Equally the influence of the "other half" of the molecule might be of great significance in its effect on the diazonium stability. This entailed a separate but allied investigation into the stability of the diazonium functional group in the presence of alternative anions.

2.5.1 Alternative Diazonium salts

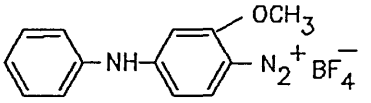
In order to obtain diazonium salts that are used in commercial formulations, several suppliers were contacted and samples from Organic Specialities and ABM Chemicals were assembled for comparative testing. These include the already described tetrafluoroborate and hexafluorophosphate salts of diazodiphenylamine. So as to reduce the number of variables, only salts with either of these two counterions were considered. The structures are as given below (23-30 and 31-35).



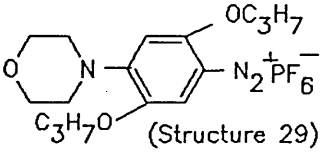
(Structures 23 and 24)



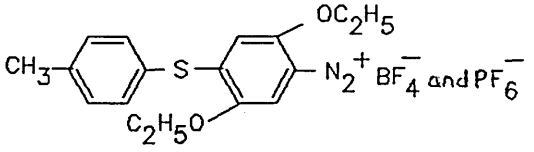
(Structure 28)



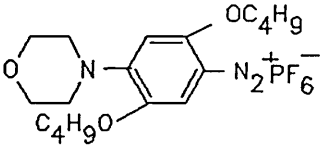
(Structure 25)



(Structure 29)



(Structures 26 and 27)



(Structure 30)

(23: Diphenylamine-4-diazonium tetrafluoroborate)

(24: Diphenylamine-4-diazonium hexafluorophosphate)

(25: 2-Methoxy-diphenylamine diazonium tetrafluoroborate)

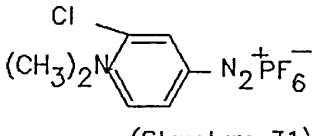
(26: 2,5 Diethoxy-4'-methyl-diphenylsulphide 4-diazonium tetrafluoroborate)

(27: 2,5 Diethoxy-4'-methyl-diphenylsulphide 4-diazonium hexafluorophosphate)

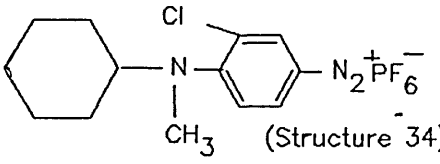
(28: 2,5 Diethoxy-4-morpholino diazonium tetrafluoroborate)

(29: 2,5 Dipropoxy-4-morpholino diazonium hexafluorophosphate)

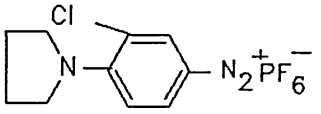
(30: 2,5 Dibutoxy-4-morpholino diazonium hexafluorophosphate)



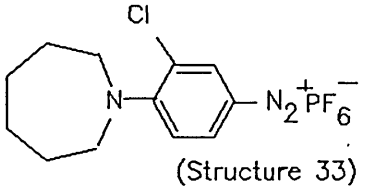
(Structure 31)



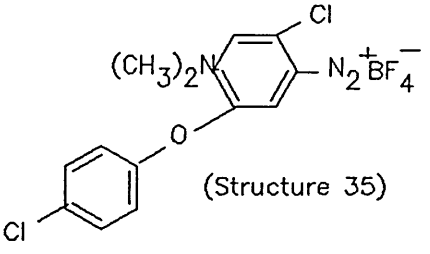
(Structure 34)



(Structure 32)



(Structure 33)



(Structure 35)

(31: 3-Chloro-4-dimethylamino diazonium hexafluorophosphate)

(32: 3-Chloro-4-pyrrolidinobenzene diazonium hexafluorophosphate)

(33: 3-Chloro-4-hexamethyleneiminobenzene diazonium hexafluorophosphate)

(34: 3-Chloro-4-cyclohexyl-methylaminobenzene diazonium hexafluorophosphate)

(35: 2-Chloro-4-diethylamino-5-p-chlorophenoxybenzene tetrafluoroborate)

The diazonium salts obtained fall into several distinct groups. Structures 23 to 25 are diphenylamine based, 26 and 27 are the same diphenylsulphide with differing counterions and 28 to 30 are 4-morpholino 2,5 alkoxy substituted benzene diazoniums that have 2,5 substituents that are in a homologous series. Structures

31 to 35 all have various nitrogen bonded substituents in the para position and a chlorine substituent elsewhere on the benzene diazonium ring.

The validity of the structures was assessed using elemental analysis and all those used gave carbon, nitrogen and hydrogen results close to theory.

Thermal Analysis and stability results

To obtain some general data on the thermal behaviour of the various compounds described above, thermal analysis by differential scanning calorimetry was carried out. The analysis was carried out directly on the sample powder. The results represent a useful starting point, but it is important to note that the thermal effects over a few minutes and a wide temperature range, do not readily translate into comparative decompositions at low and constant temperatures over several weeks in a solution of other chemicals. For consistency each sample was analysed over an identical temperature range (30 to 300 °C) and at the same rate of temperature increase (10 °C/min.).

Measurements of the temperature at the onset of an exotherm (as the sample began to decompose), of the temperature at the peak maximum and of the heat evolved during the exotherm (from the peak area) were recorded. The results are given in the table below. The thermal behaviour varies widely. Results for the energy output during decomposition are probably not as relevant to the stability investigation as the results for the temperature of onset of decomposition. Any heat generated during decomposition of coating solutions or plate formulations would be dissipated by the sample matrix. One point of note is that the sample with the highest energy output during decomposition is the sample of lowest molecular size (structure 31), which only contains one ring. This is as would be expected, although due to the differences in molecular structure, there is not a particularly good correlation for the group as a whole. A further problem

with comparing the energy figures is that many of the samples begin to melt just before, or probably during, decomposition. It was not possible to differentiate between the contributions to the total energy change from the exothermic decomposition and the endothermic melting.

Table 16: Thermal analysis results for various diazonium salts.

STRUCTURE	ONSET °C	PEAK EXO.°C	ΔH J/gm.
23	145	154	486
24	148	170	295
25	181	188	405
26	154	160	239
27	155	159	227
28	113	134	437
29	137	149	442
30	127	139	387
31	133	136	644
32	129	136	478
33	113	138	400
34	113	138	510
35	136	142	441

Two examples of the thermograms obtained are included below (figures 20 and 21).

These are two extreme results in several respects. That of structure 25 has the highest onset (181 °C) and peak decomposition temperatures and decomposes over a narrow temperature range . In contrast that of structure 32 has a much lower decomposition onset temperature (113 °C) and gives a much broader melting/decomposition thermogram.

The widely varying results in the above table indicated that large differences in thermal stability might be expected. There was also the possibility that the diazonium salts that only began to decompose at relatively

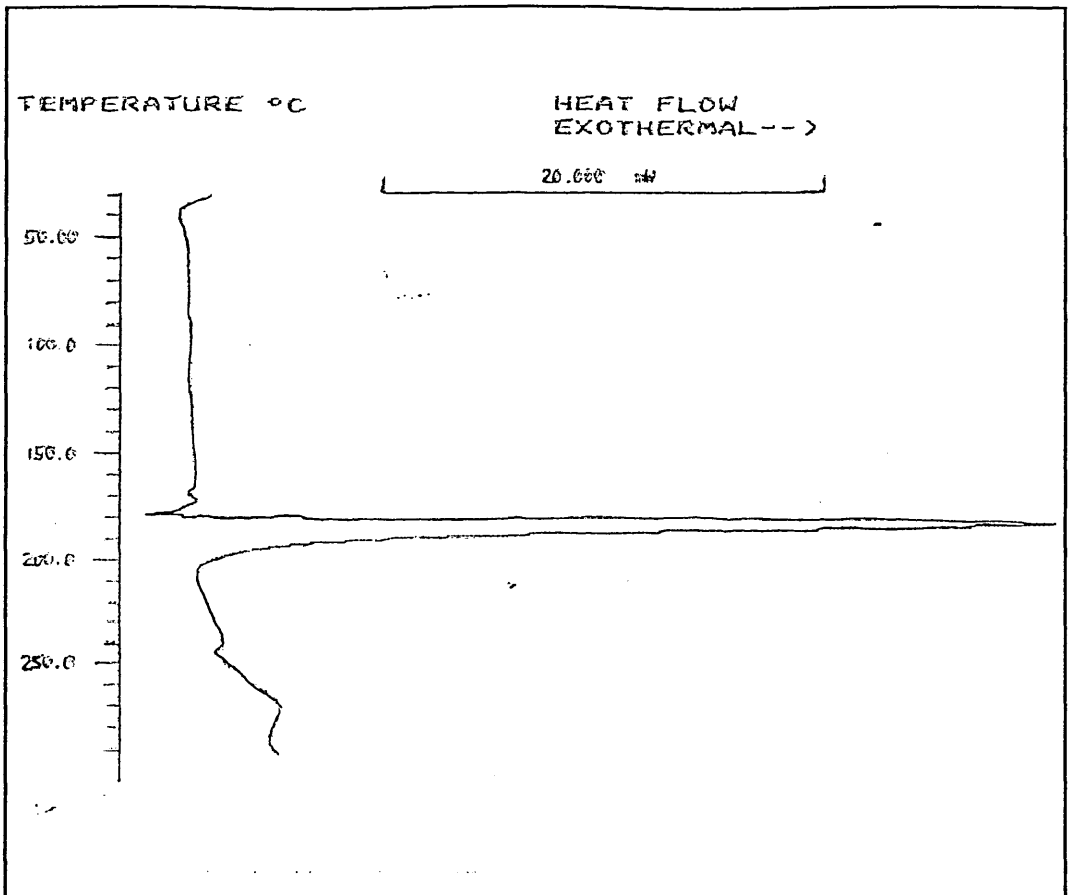


Figure 20: Thermogram of Structure 25

high temperatures would prove to be more stable in coatings and plate formulations.

The same group of compounds was tested for coating solution stability in 10 % p-cresol solution in acetone at 50 °C. The decomposition tests were carried out using ultra-violet/visible spectroscopy at the wavelength of maximum absorption (λ,max.), the higher wavelength peak being used if there was more than one absorption band. This method of analysis was used because UV/visible spectroscopy gives accurate, rapid comparative results for such simple matrices with relatively little method development work, even for a wide range of diazonium types.

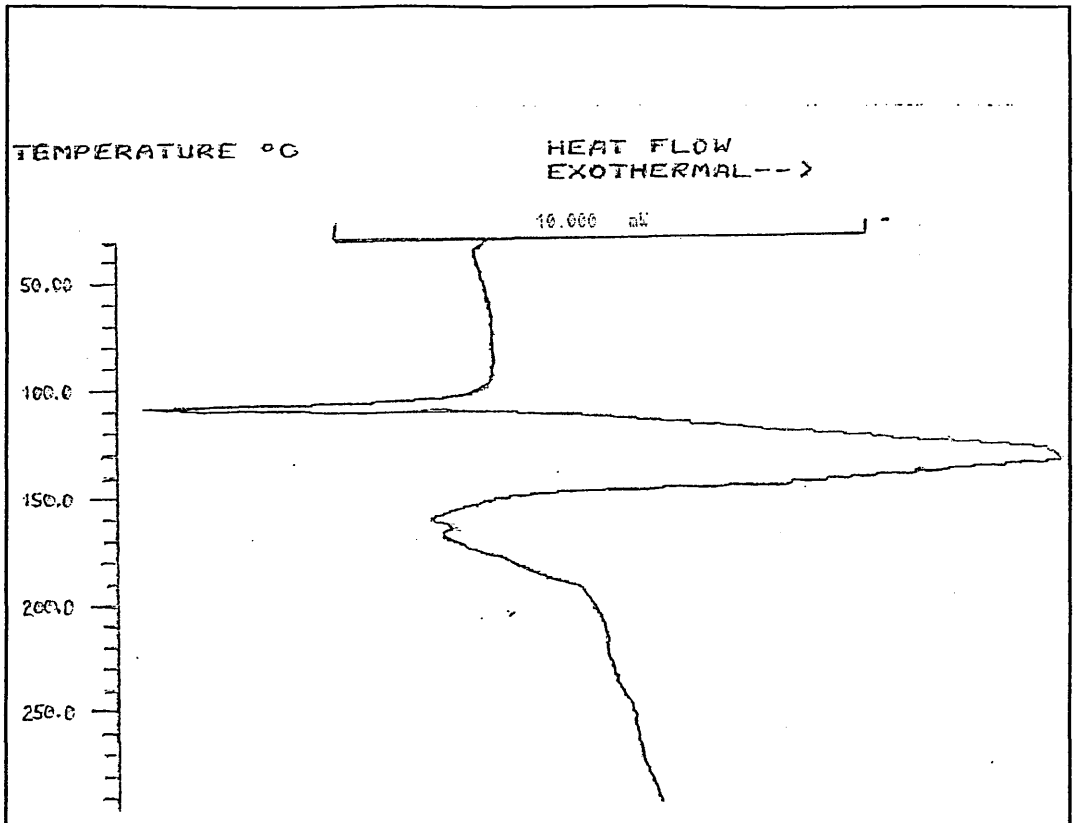


Figure 21: Thermogram of structure 33

Table 17: Stability and λ max. for diazonium salts.

Structure	λ max.(nm)	% Decomposition
23	378	20
24	378	33
25	368	10
26	404	19
27	403	31
28	402	40
29	403	37
30	402	40
31	394	40
32	394	43
33	397	57
34	400	47
35	405	53

The positions of the λ max. do not correlate with stability or thermal data in Table 16. It had been hoped that absorption at longer wavelengths would signify a greater contribution from a quinoid structure and that this would impart greater solution stability. As all the diazonium salts under test had significant absorption at these longer wavelengths, the differences observed are probably due to other minor conjugation effects.

The λ max. absorptions for the two pairs of structures 23 and 24, and 26 and 27 that differ only in counterion are identical, showing that the tetrafluoroborate and hexafluorophosphate counterions do not affect the conjugation within the cation. Both pairs provide further evidence of the improved stability of diazonium salts with a tetrafluoroborate anion compared to hexafluorophosphate (as discussed in section 2.3.3).

Comparison of the stabilities shows that most of the additional diazonium salts have inferior stability to the diazodiphenylamine that has been used as the model for this investigation. Of very similar stability to the diazonium diphenylamines are the diphenyl sulphides. There is only one diazonium salt that shows markedly improved stability, structure 25. This is an ortho-methoxy substituted diazodiphenylamine. The improved solution stabilities are broadly in line with those that might have been predicted from the relative order of onset of decomposition temperatures in Table 16, at least as far as the most stable compounds are concerned. Structure 25 had the highest decomposition onset temperature and is the most stable in solution. The diazodiphenylamine and diazodiphenylsulphide samples both had high decomposition onset temperatures and are comparatively stable in the coating solution. Although there is a rough correlation, it is by no means exact. There is no evidence for the anion stabilisation for example, from the thermal analysis alone.

The commercially available diazonium salts studied are all stabilised by incorporating electron donating

substituents in the para position, and sometimes in the ortho position as well. Thus either nitrogen, sulphur, oxygen or chlorine bonded substituents are used that have lone pairs of electrons that can interact via a mesomeric effect with the diazonium aromatic ring. This interaction with the aromatic delocalised electrons will reduce the charge of the diazo group. The additional stability of the diphenylamine and diphenylsulphide based diazonium compounds is probably related to the additional stabilisation from the phenyl substituent. Structure 34 has a phenoxy substituent but this is meta to the diazonium group which will prevent mesomeric interactions, hence giving inferior stability.

The additional stability conferred by the ortho methoxy substituted diphenylamine is due to its electron donating properties, which will re-enforce the effect of the phenylamino substituent. It is likely that other electron donating substituents ortho to the diazo will have a similar effect.

As mentioned in section 1.8.3, Becker et al[30] have shown that reaction by heterolytic or homolytic reaction occurs depending on the relative amounts of energy required for internal or external electron transfer. Transfer internally from the aryl group results in the heterolytic mechanism predominating, while transfer from an external donor such as the solvent or anion results in the homolytic free radical mechanism. In general terms the capacity for transfer from an external donor will increase the greater the ionisation potential of the donor and the greater the electron affinity of the diazonium salt (the acceptor). In an attempt to quantify the electron affinity of the diazonium cation, a polarographic study of the diazonium salts was carried out.

Polarographic Analysis

The diazonium salts studied would be expected to readily accept an electron and undergo reduction in aprotic solvents according to the following scheme[80].

$$ArN_2^+ + e \rightarrow ArN_2^{\cdot} \rightarrow Ar^{\cdot} + N_2$$

(Scheme 27: Reduction reaction of diazonium salts in aprotic solvents).
This is in contrast to the reduction to phenylhydrazines observed in aqueous media (scheme 26).

The group of diazonium salts already studied for solution stability and by thermal analysis were investigated using pulsed square wave voltametry. Solutions in acetonitrile were used as this is a common aprotic solvent used for this technique. The solutions were buffered and scanned from +1 to -1 volt to detect reductive reactions. Initial results using a graphite electrode were disappointing as no significant reductions were detected. Switching to a gold electrode gave improved results. These were reproducible provided the solution was purged with nitrogen and the electrode was cut to provide a clean surface after about every four sample runs.

The integrated scans gave peaks when a reduction was detected as shown in the example below. The second featureless trace on which the sample scan is superimposed is a blank of buffered solvent only.

The diazonium salts all gave a reduction peak at varying voltages, although the traces were otherwise very similar. The half-wave potential results ($E_{½}$ corrected to standard calomel electrode), with the solution stability results for comparison are given in the table below.

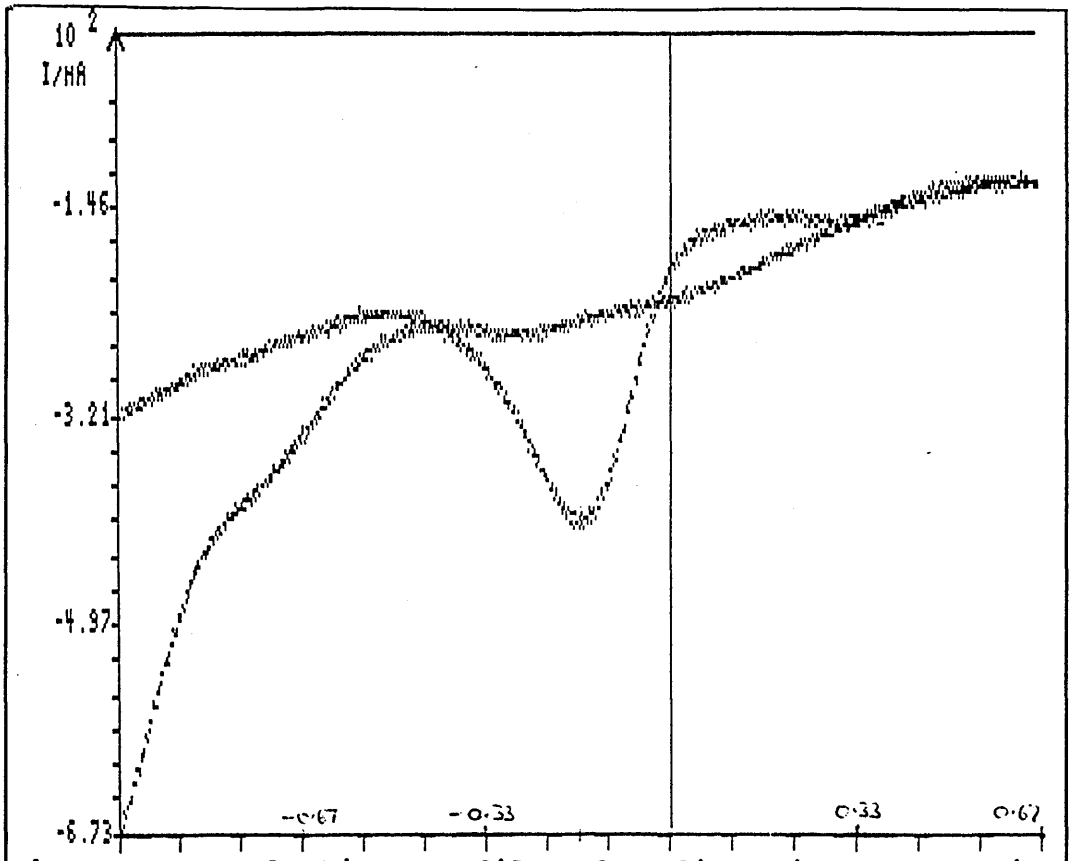


Figure 22: Reduction profile of a diazonium salt using pulsed square wave voltammetry and a gold electrode.

Table 18: Stability and half-wave potentials for a range of diazonium salts.

Structure	$E_{1/2}$ vs.SCE(V)	% Decomposition
23	+ 0.116	20
24	+ 0.096	33
25	- 0.044	10
26	+ 0.156	19
27	+ 0.123	31
28	- 0.054	40
29	- 0.069	37
30	- 0.054	40
31	+ 0.206	40
32	+ 0.016	43
33	+ 0.196	57
34	+ 0.176	47
35	+ 0.131	53

It was expected that diazonium salts with the most electron donating substituents would have the more negative half-wave potentials because their diazo groups were more difficult to reduce. Furthermore the more difficult the diazonium salt was to reduce, the more stable it might be expected to be. From the table above there is no obvious correlation between the half-wave potentials and the stability results. The compound of structure 25, which gave the most stable solution, has a more negative half-wave potential, and some of the most unstable compounds do have high positive potentials. However, the group of similar structures 28-30, each having a morpholino substituent, is the obvious exception. These are of fairly poor stability but with strongly negative half-wave potentials.

Although polarography may give some general indication of which compounds are likely to gave more stable coating solutions, its use is clearly obscured by the influence of other factors. One of these will be the influence of the counterion.

2.5.2 Alternative Counterions

The previous section considered the variations in stability that were encountered from a range of diazonium salts and some of the likely causes of the differences observed. Although the diazonium salt cation is the part of the molecule that is the centre of any decomposition, the anion may have considerable impact on the rate of decomposition. Indeed a difference in the stability of tetrafluoroborate compared to hexafluorophosphate diazonium salts has already been encountered in section 2.3.3. This difference provided the main impetus for the preparation of a wide range of counterions to see if any offered improved stability beyond that of the tetrafluoroborate.

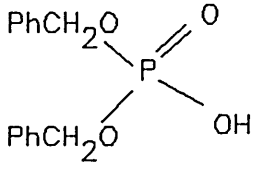
To avoid difficulties in interpreting the results, the cation was kept constant and the anion only was

varied. The cation chosen was the diazodiphenylamine that has been used throughout this study. A sample of the bisulphate salt of this compound was used for the preparations as this is readily water soluble. The technique is described in more detail in section 3. Generally the method consisted of adding to an aqueous solution of the potential counterion (as the sodium salt, or the acid), an aqueous solution of the diazonium bisulphate salt. If the ion exchange was successful and the solubility of the product in water was low, the product precipitated out of the water and was filtered off. If no precipitate could be isolated, the solution was extracted into chloroform and the extract evaporated down to give the ion exchanged product.

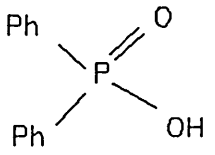
The initial preparations consisted of attempting to make diazonium salts of commonly available organic anions that were potentially soluble in the coating solvent. Such anions should also give a diazonium salt that would precipitate from water, or be easily extracted from it with chloroform or other water-immiscible solvent. In many cases these proved to be difficult criteria to meet. Salts such as sodium stearate and similar long chain alkane compounds were insufficiently water soluble for ion exchange to occur. At the other extreme, many ion exchange reactions if they occurred at all, gave only water soluble products that would neither precipitate from water nor extract into chloroform. This included a large group of anions such as: formate, acetate, cyanoacetate, phosphate, phosphonate, methylphosphonate, benzylphosphonic acid, naphthylphosphonate (added as the disodium salt) and various phosphites. Several phosphorus containing compounds were included because of the link with hexafluorophosphate and the large number of phosphorus compounds available that included different organic species.

The phosphites as a group did not ion pair easily, probably due to their being extremely weak acids under aqueous conditions. Groups such as mono substituted

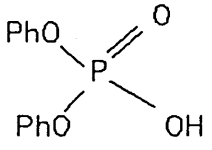
phosphates having two acidic protons were too water soluble. However dibenzylphosphate, diphenylphosphinic acid and diphenylphosphate (structures below) were less water soluble but sufficiently so for the ion exchange to be carried out and gave precipitates of the diazonium salt which could be easily extracted and purified.



(36)



(37)



(38)

(36: Dibenzylphosphoric acid)
(37: Diphenylphosphinic acid)
(38: Diphenylphosphoric acid)

The other major group of compounds studied was the sulphonic acids. This was again partially dictated by the availability of a large group of compounds with varying substituents, but more importantly by the literature findings that compounds such as arenesulphonates can give diazonium salts that are more stable solids than those of mineral acids (see section 1.8.4).

In the case of some of the more water soluble ion exchanged products, none of the product precipitated at room temperature. If the solution was warmed slightly for a short time coagulation occurred and improved ion exchange as indicated by precipitation of the product. The solution was only warmed to about 30 °C for 15 minutes and there was no evidence of any decomposition. Other slight variations on the general method were necessary in some cases to achieve ion exchange. For added salts that were not particularly water soluble, the addition of some acetone to the aqueous solution of the diazonium bisulphate salt assisted solubility and hence ion exchange.

The preparations were initially carried out on a limited number of compounds, but the number was extended

in an attempt to explain some of the stability differences. Stability tests were carried out over 7 days at 50 °C in 10 % w/v cresol novolak solution and decomposition measured by UV/vis. spectroscopy. For clarity all the results of the compounds successfully exchanged are summarised in the table below.

Table 19: Stabilities of diazodiphenylamine salts having a range of different counterions.

Counterion	% Decomposition
Hexafluorophosphate	42
Tetrafluoroborate	33
Lauryl sulphate	45
Methane sulphonate	19
Pentane sulphonate	24
Heptane sulphonate	28
Toluene sulphonate	30
Naphthalene sulphonate	23
Trifluoromethylsulphonate (TFMS)	14
Trifluoroacetate	34
Trichloroacetate	40
Tribromoacetate	45
Benzoate	35
Dibenzylphosphonate	79
Diphenylphosphonate	95
Diphenylphosphate	63
Tetraphenylborate	90

The additional phosphorus compounds all gave diazonium stabilities significantly worse than the hexafluorophosphate already studied. Also particularly poor was the tetraphenyl borate. This ion exchange reaction was unusual in that the diazonium salt solution began to bubble showing decomposition during the ion exchange process. The resulting ion exchanged product was of relatively poor elemental analysis (the nitrogen figure was low, as might

be expected), but a solution stability was carried out for completion.

The simple halogenated carboxylic acids gave diazonium salt stabilities equivalent to the extensively studied tetrafluoroborate and hexafluorophosphate salts. All the sulphonates gave improved diazonium stabilities. The most stabilising anions were the short chain aliphatic sulphonates, the shorter the chain the better the diazonium stability. This could be caused by having statistically fewer hydrogen atoms readily available for hydrodediazoniation reactions. The most stable diazonium salt under these test conditions was the trifluoromethyl sulphonate. This seems to be in line with the link between fewer hydrogen atoms in the sulphonate anion giving improved diazonium stability.

Improvements in diazonium stability of this type are of interest for the stabilisation of polymers and for diazonium salts used as acid release agents. Using diazodiphenylamine with a TFMS counterion gave a good colour change on exposure in a simple plate formulation incorporating an acid sensitive dye.

2.6 STABILISATION BY ALTERNATIVE SOLVENTS AND ADDITIVES

During this investigation several changes to the initially proposed positive working plate system have resulted in improved diazonium stability. The detrimental effect of water, the beneficial use of monomer free novolak and alternative diazonium salt cations and anions have all been shown to be ways of influencing diazonium stability. However other possibilities have also been investigated. These are the solvent itself, and the addition of certain stabilising compounds. The influence of these compounds will be considered in this section.

2.6.1 Alternative Solvents

Thus far although the diazonium salt stability has been examined under varying conditions using a range of diazonium cations with various anions, the effect of the major component of any coating solution has not been reported; this component is the coating solvent. Apart from some initial investigations in section 2.2.3 which showed some minor variations in diazonium salt stability in the presence of different ketones, other solvents have not been considered. Solvent change is likely to have much less impact on the stability of the final printing plate as the vast majority of it is removed during a short drying stage. Indeed one of the prerequisites of a satisfactory coating solvent is that it should be quick drying so that the printing plates can be cut and packaged immediately after production.

The level of acetone remaining on the printing plate surface was measured using GLC and was found to be only about 8 mg./m^2. Less volatile solvents gave higher residues of up to 80 mg/m^2, but gave inferior coating appearance with uneven coating weights.

However it was necessary to examine the solution stability in a range of alternative solvents even though many of these would not be suitable as coating solvents for reasons such as low volatility or poor solubility of other coating components. This examination was carried out in order to discover what solvent factors did have an effect on diazonium stability so as to provide information for coating solvent selection.

In order to simplify the interpretation of any results, as few variables as possible were introduced to the experimental scheme. The diazodiphenylamine hexafluorophosphate salt was used for all the trials.

A range of solvents were chosen that were of widely differing structure and which might therefore be expected to have differing effects on diazonium stability. From earlier discussion of the reaction mechanism, it was clear

that the decomposition reaction in acetone of this compound proceeded largely by a radical mechanism involving homolytic schism of the diazo group from the aromatic ring. This was facilitated by donation of an electron from the matrix. If the matrix is kept to just the diazonium salt in a solvent, this electron would have to be supplied from either the solvent or the anion for radical decomposition to proceed. One factor that was initially investigated was the conductivity of diazonium salt solutions.

Table 20: Conductivity measurements in μS/cm.of diazodiphenylamine hexafluorophosphate in various solvents at different concentrations (in gm/100ml).

Solvent	0	0.01	0.02	0.04	0.08	0.16
Water(Dist)	3	32	64	119	222	404
Acetone	0	56	97	196	343	630
MEK	0	45	73	130	240	455
Methanol	13	37	85	127	238	445
Acetonitrile	0	59	102	193	381	748
Unst. THF	0	4	5	8	12	21
DMF	3	28	44	83	159	315
2-methoxy ethanol	1	11	22	39	72	131
Ethanol	0	17	29	59	94	166

Use of other solvents such as toluene, chloroform and dioxane was attempted but gave insufficient diazonium salt solubility. Measurements were carried out using a simple conductivity probe at 22 °C. In each case in the table above the increase in conductivity with concentration is a linear relationship. There is a wide range in conductivities from the low levels encountered with unstabilised tetrahydrofuran (THF), to high levels for acetonitrile and acetone. These differences are due to complex effects due to the inherent polarity of the solvent and the degree of solvation of the salt cation and anion.

Stability tests were carried out using the solvents in the table above, excluding water. The latter was omitted because the solution was cloudy indicating that the salt was only partially soluble and the adverse effects of low levels of water have already been investigated (in section 2.2.3).

Trials were carried out with the diazonium salt in solvent only and also in 5 % novolak solution (this lower concentration was used because of solubility difficulties in some of the solvents, especially methanol).

Table 21: Stability comparisons for diazonium in various solvents and in cresol novolak solution compared to conductivity.

Solvent	% Decomp. no novolak	% Decomp.in 5 % novolak	μS/cm. 0.16g/100
Acetone	15	35	630
MEK	19	47	455
Methanol	70	65	445
Acetonitrile	12	18	748
Unst. THF	74	70	21
DMF	85	62	315
2-methoxy ethanol	25	34	131
Ethanol	23	38	166

These results reveal a number of interesting points. Firstly they highlight that the solvent will have a dramatic impact on diazonium stability, more so than most of the other variations considered so far. This is because of their over-riding contribution to the matrix, the solvent being the vast bulk of the matrix. The results are also important because they show that solvents differ greatly in their effect on the diazonium salt stability. Although acetone happens to provide one of the most stable matrices, that of acetonitrile gives even greater stability. In contrast, solvents such as DMF, methanol and THF give very poor stability results.

Comparing the results with the conductivity figures, there is no clear correlation. Although acetonitrile and acetone give good stabilities and have high salt solution conductivities, the THF solution has a low conductivity and gives inferior stabilities. However, this relationship does not hold particularly well for DMF. Other solvent parameters are clearly having an influence on the diazonium stability.

Solvent polarity indices, such as those of Reichardt[81], have been consulted. Once again there is no correlation between the various solvent parameters and stabilities. The donor numbers devised by Gutmann[46] are thought by Zollinger to give some indication of the chance of dediazoniation via a radical mechanism. From the limited figures available, there is a possible correlation. The low figures for acetonitrile and acetone (14.1 and 17.0 respectively), which gave good diazonium salt stabilities, contrast with the higher figures for THF (20.0), DMF (26.6) and indeed water (33 approx.). The quoted figure for methanol is given as greater than 19.1. However Zollinger also states that "these reactions exhibit a surprising and apparently inexplicable variety of mechanisms: there is not one heterolytic and one homolytic decomposition pathway but several"[29].

This latter observation is born out in the above table of results when the influence of the novolak resin is considered. Throughout this investigation, novolak has been shown to promote increased diazonium decomposition. Although this is generally still the case, the novolak can improve the diazonium stability for solvents where the level of decomposition is particularly high in solvent alone. This was most marked for DMF, the other cases gave only slight improvements, within experimental error, which meant that decomposition was at least no worse with the novolak. This may be due to the much higher donor properties of DMF being reduced in effectiveness by solvation of the diazonium salt by the novolak oligomers.

In conclusion, solvents of low donor properties according to Gutmann's indices are most likely to give stable diazonium salt solutions. However, the effects of solvent changes on diazonium salt decomposition are complex and highly significant. As mentioned previously, from a practical lithographic printing point of view, there are other factors that would have to be taken into account before any solvent change could be introduced for on line plate production. Not least would be solvent toxicity, which would rule out acetonitrile despite its technical improvements.

2.6.2 Addition of stabilisers

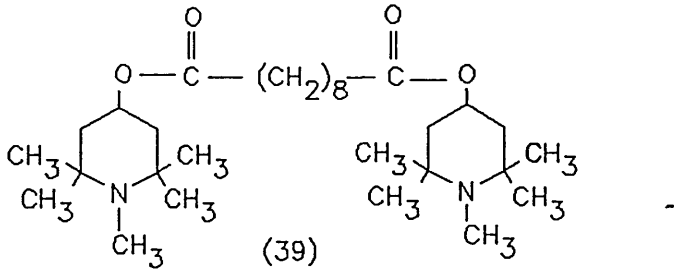
Various compounds were considered as worth investigating to determine if they imparted any improvement in the stability of diazonium salt solutions. These fell into three groups; the Tinuvin series of photochemical stabilisers, radical traps and the theophylline derivatives. Nitrogen purging was also investigated.

Tinuvin Stabilisers

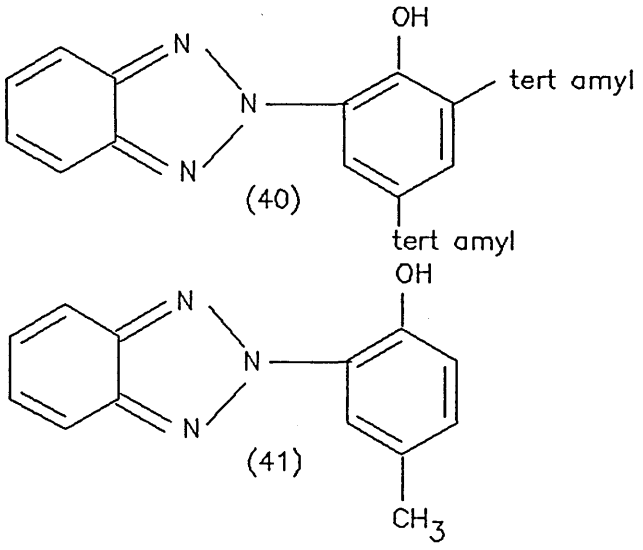
The Tinuvin stabilisers are marketed by Ciba-Giegy as stabilisers for Ultra-Violet sensitive systems. Four were selected for investigation. One was Tinuvin 622 which is described as a "polymeric sterically hindered amine derivative". This proved to be insufficiently soluble in acetone for stability testing. The other three were tested in coating formulations. Their structures are given below.

These stabilisers were incorporated at a level of 1 % w/v in acetone solutions containing 10 % cresol novolak and 0.2 % diazodiphenylamine hexafluorophosphate.

No significant improvement in the stability of the diazonium salt was observed. This is probably because the stabilisers function as UV stabilisers by absorbing any incident radiation rather than inhibiting any



(39)



(40)

(41)

(39: Tinuvin 292)
(40: Tinuvin 328)
(41: Tinuvin P)
decomposition processes.

Radical Traps

Having shown that the diazonium decomposition reaction proceeds predominantly via a radical mechanism, an attempt was made to slow down this process by adding radical inhibitors. Three compounds were investigated: iodobenzene, butylated hydroxytoluene (BHT) and diphenylamine. The first two were used because they have received some mention in diazonium literature and diphenylamine because it is not only a radical trap but is formed during the diazodiphenylamine reaction.

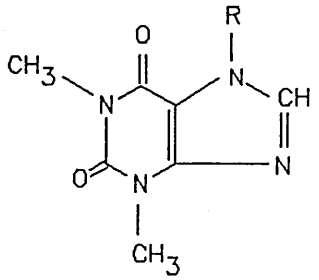
They were incorporated in stability solutions of the type used for the Tinuvin tests above. Iodobenzene made no significant difference to the decomposition rate (this is

in line with Zollinger's observations on a different diazonium compound that decomposed via a radical decomposition mechanism[29]).

Diphenylamine and BHT both gave inferior diazonium stabilities. These results are disappointing but perhaps not surprising given the role of diphenylamine in coupling with aryl radicals, and the similarity of BHT to the cresols that promote decomposition in acetone solution.

Theophylline Stabilisers

A recent patent[82] refers to the use of theophylline stabilisers for use in aqueous emulsions in lithographic plate making. No information is given as to the likely mechanism in the patent. Correspondence with the author indicates that the theophyllines prevent dimerisation of diazonium resins, though the exact mechanism is unknown. The patent recommends that they be incorporated with other stabilisers in systems that function via the cationic polymerisation of epoxides (see section 1.8).
Both a chloro and propyl theophylline stabiliser were investigated in novolak based systems.



R=Cl or propyl

(42:Theophylline stabilisers)

At a 10 fold molar excess on diazonium salt, these stabilisers gave no stability improvement, and have not been investigated further.

Nitrogen Purging

Reference is made in section 1.8.3 to the reversibility of the decomposition of diazonium compounds,

in particular in the presence of high pressures of nitrogen. The pressures quoted are very large, of the order of 300 atmospheres. It was thought worthwhile to investigate the effects of samples purged with nitrogen and sealed during the stability test. There was also the possibility that exclusion of oxygen would make radical processes proceed more efficiently giving increased decomposition.

In the event, nitrogen purging made no difference to the stability of the diazonium compared to either a solution that was not purged nor to a solution purged with air. This is probably because the concentration of nitrogen at the site of decomposition is insufficient to reverse the decomposition process. As the reaction already proceeds through a largely radical reaction mechanism, exclusion of oxygen will have less impact. It has been reported[29] that similar experiments in methanol divert the reaction mechanism from a heterolytic to a homolytic pathway.

Conclusion

All additives studied either give no significant improvement in the rate of diazonium decomposition or actually make it worse. One kind of additive that will be considered separately is complexation by multidentate polyethers, since these gave more encouraging results as explained in the next section.

2.7 HOST-GUEST COMPLEXATION

In section 1.8.4 various literature references to improving the stability of diazonium salts were mentioned. The intriguing phenomenon of the ability of certain cyclic ethers to fit around the diazo group like a collar around a neck was explained in section 1.8.4 and detailed in references 53-61. The cyclic ethers are the crown ethers,

particularly 18-crown-6. The form of the complexation is as shown in structure 14.

It was found that certain crown ether-diazonium salt systems gave evidence of complexation by NMR changes and UV absorption shifts. When complexation occurred, improved thermal stability was conferred on the diazonium salt.

This is an area of active research work at present. One recent study has used fast atom bombardment mass spectrometry to study the bonding between the complex and the aryl diazonium cation[83]. There is evidence of transfer of acid protons from the aryl group to the basic crown oxygens. They also observe that electron-donating substituents will decrease the positive charge on the diazonium and decrease complexation with the crown ether. Other workers [60] have similarly observed that para amino substituents have caused almost total loss of stability of the complex. This has unfortunate implications for the diazonium salts which form the subject of this report, which have electron donating para substituents.

The other recent report of interest investigated complexation with 15-crown-5 ether[84]. This had too small a cavity to allow insertion complexes but did give evidence of weak complexation of a charge transfer type.

These crown ether complexes were investigated in this study to see if they might be sufficiently effective even with para amino substituted diazonium salts to impart stabilisation in lithographic matrices.

2.7.1 Effect of crown ethers in lithographic systems

Only three crown ethers were available commercially (from Aldrich). These are 12-crown-4, 15-crown-5 and 18-crown-6. Each of these was incorporated in a stability solution containing 10 %w/v cresol novolak in acetone at 5 times molar excess on diazodiphenylamine hexafluorophosphate. A portion of the same solution without crown ether was incorporated in the test regime as a blank. The results are shown in the following table.

Table 22: Crown ether stabilisation of diazodiphenylamine.	
Crown ether added	% Diazonium decomposition
None	39
12-crown-4	51
15-crown-5	46
18-crown-6	18

The results show some deterioration in the diazonium stability with 12-crown-4 and 15-crown-5, but a great improvement when using the 18-crown-6 ether. The improved stability of the 18-crown-6 ether compared to the others has been noted by other workers in the field[57,59,83]. This is thought to be related to the size of the cavity provided by the ether; those of 12-crown-4 and 15-crown-5 being too small to accommodate the diazonium cation.

This result was both surprising and encouraging. It had been expected that any complexation with a diazonium salt containing electron donating substituents would be small[58,60], giving rise to only a marginal stability improvement.

The degree of stability improvement was investigated further to see if the crown ether addition could be optimised. Similar solution stability trials to those described above were carried out but varying the 18-crown-6 ether excess from zero to five fold.

As a measure of the degree of complexation, the hypsochromic shift in the diazonium absorption in the ultra-violet visible spectrum was also measured. The diazonium salt gives a strong absorption at 378 nm with no crown ether present. The position of the maximum absorption gradually falls as crown ether is added to a level around 363 nm, some 15 nm below the initial value. These results on the dual effects on the position of absorption and diazonium stability are shown graphically below.

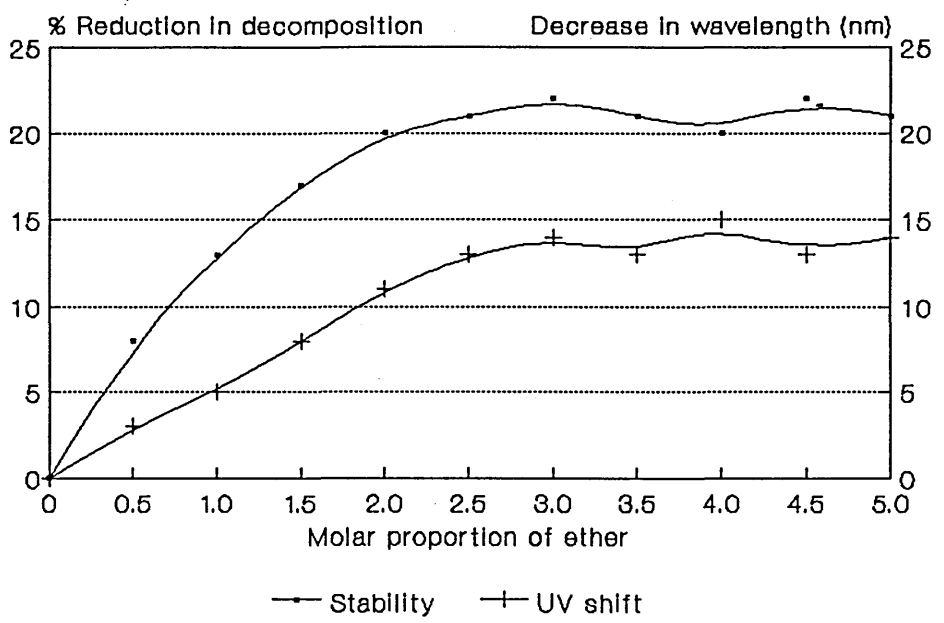


Figure 23: Effect of 18-crown-6 ether concentration on diazonium stability and the shift in the position of the uv absorption maximum.

The results indicate that there is an improvement in the diazonium stability up to a crown ether level about two and a half times the molar concentration of the diazonium salt. Beyond that level the stability improvement has levelled off and no further stability is obtained for further crown ether additions.

The shift in the position of the UV absorption maximum follows a similar pattern, which is good evidence for the degree of complexation having a direct influence on the diazonium stability.

Similar tests were carried out using the diazodiphenylamine tetrafluoroborate salt. In this case there was both less evidence of complexation and less improvement in the stability results. Comparable figures with the hexafluorophosphate salt were a stability improvement from 39 to 18% decomposition and a wavelength shift of 15 nm for the hexafluorophosphate compared to a 39 to 28 % decomposition and wavelength shift of 10 nm for the same molar proportion of tetrafluoroborate. Similar

differences in the complexation of these two anions have been observed by other workers[68]. This is thought to be due to reduced ion pairing between the diazonium cation and the hexafluorophosphate anion compared with the tetrafluoroborate. Hence in the hexafluorophosphate case, the more electropositive diazonium cation will have a greater attraction for the crown ether.

2.7.2 Effects of other polyethers

Work by Bartsch and Juri[61] has, as explained in section 1.8.4, cast doubt on a rigid interpretation of the "collar and neck" analogy as a means of visualising the mode of complexation of diazonium salts by crown ethers. They utilised a series of polyethylene glycol ethers known as glymes that were not cyclic but were shown to give similar effects as the crown ethers. However, from their results, the most effective glymes were those whose conformation most closely simulated that found in the cyclic ethers. The structure of the glymes was sufficiently close to that of the crown ethers, such that complexation through a combination of electronic and structural configuration factors explained the formation of the complexes.

Their observations were important in that they opened up the way for commercial utilisation of stabilisation by these complexes using cheap, readily available compounds such as the Carbowax series of polyethers.

Stability trials were carried out incorporating polyethylene glycols of varying molecular weight in diazodiphenylamine hexafluorophosphate and novolak solutions. Comparative testing was carried out with a portion of the stock solution with no added crown ether or polyethylene glycol (Table 23).

Table 23: Diazonium stability comparisons in the presence of polyethylene glycols and 18-crown-6 ether.	
Added species	% Decomposition
None	39
18-crown-6	18
Polyethylene glycol MW 12600	23
Polyethylene glycol MW 8650	21
Polyethylene glycol MW 960	25
Polyethylene glycol MW 194	31

These results show that the higher molecular weight polyethylene glycols (PEG) do give some stabilisation of the diazonium salt. The stabilisation is less apparent for lower molecular weight additions. Although the stabilisation is not quite as good as using the 18-crown-6 ether, the relative cost of the reagents would make use of PEG more practical on a large scale. It should also be noted that the above stabilisations were using equal weights of the PEGs and crown ether, rather than molar excesses. This was done to make comparisons between the PEGs more straight forward.

2.8 POLYMERIC DIAZONIUM SYSTEMS

The discussion so far has been solely concerned with understanding the way in which monomeric diazonium salts decompose and the various factors that influence the rate of that decomposition. It has been shown that there are a number of parameters that can be used to improve the stability of monomeric diazonium salts in positive working coating solutions. As explained in section 1.7, diazodiphenylamine salts were used in this study not only to improve their stability in coating solutions and plates but also as a model for the investigation of polymeric diazonium salts in negative working plate systems.

In this case the diazonium polymer forms the bulk of the formulation. There is no requirement for the anion to

function as a Lewis acid which gives greater scope for the use of alternatives.

As expected, the analysis of the polymer proved much more difficult than the corresponding monomer. A polymer as shown in structure 9 (P. 31) was used for the tests.

The problem with the analysis is that the polymer chain will have a series of pendant diazonium groups. Under adverse conditions these diazonium groups will decompose at random in any polymer chain. However it only needs a few of the diazonium groups in any polymer chain to decompose to render that portion of the polymer insoluble. This was demonstrated by stability trials when increased levels of diazonium decomposition were detected in solution compared to monomeric systems. It was found that the polymeric stability solutions invariably contained large amounts of precipitate which on analysis by infra-red spectroscopy had about half of its original diazonium character intact.

Given the difficulties in obtaining an accurate measure of the diazonium decomposition, another technique was used. This was gel permeation chromatography(GPC). This is described in section 3.11. The diazonium polymers could be analysed by this method provided that the decomposition had not proceeded beyond about 10 % of the diazonium groups. Beyond this low level, precipitation again rendered results inaccurate. However even this was problematical in that the reactive diazonium salt groups adhered to the styrene divinyl benzene column packing giving variable results. Satisfactory comparative data was only obtained using aqueous GPC column packings and an eluent containing a mixture of THF, water, acetic acid and sodium lauryl sulphate.

Taking the initial molecular weight as 100 %, the following results were obtained for the effects of water addition and use of trifluoromethyl sulphonate(TFMS) counterion in place of a proprietary organic sulphonate. These were used because earlier work had shown the

detrimental effect of water additions and benefits of TFMS counterion on monomeric diazonium salt stabilities.

Table 24: Effect on molecular weight of diazonium polymer after 2 days at 40 °C in acetone solution.

Variation on standard	% Molecular weight increase
Standard	15
2% v/v water added	55
TFMS salt used	5

The results bear out the findings on the monomeric versions of the same compounds and show that the results obtained earlier form a good basis for improvements in the stability of polymeric diazonium compounds. These observations will form the foundation of a more extensive study of improvements to the stability of polymeric diazonium compounds in coatings to be undertaken outside the work reported in this investigation.

2.9 DIAZONIUM STABILITY ON PLATES

The products identified from diazonium decompositions from positive working plates and corresponding coatings were used in section 2.3 to elucidate the likely mechanisms. This work led to defining a range of possible alternative techniques to provide improvements in positive diazonium coating stability. The implications of these techniques have been examined further as a means of extending plate shelf-life.

2.9.1 Positive Plates

To avoid extensive repetition of the results obtained for coatings, plate stability tests can be summarised as showing that the same factors that influenced coating solution stability also effect the plate stability. The trifluoromethyl sulphonate salts again gave improved shelf life compared to the tetrafluoroborate,

hexafluorophosphate and other anions. Similarly the same order of stability for different diazonium cations was observed for the various alternatives studied, with the ortho methoxydiazodiphenylamine the most stable.

Provided the plates were prepared from fresh coating solutions, there was no influence detected from the solvent used. This is because the solvent is removed, as described in section 3.10, prior to plate storage. Analysis by GC, as mentioned in section 2.6.1, for the level of residual solvent showed that a plate prepared from acetone had less than 10 mg/m^2 remaining.

Also of interest were the effects of humidity and the plate wrapping used. As shown in 2.2.3, water in the coating solution has a major detrimental effect on diazonium stability. For the comparative stability tests mentioned above, plates were stored wrapped in black paper in conventional ovens over a period of days or weeks at 30 °C. When the decomposition rate of diazonium salts was compared in humidity controlled ovens and normal ovens, a large difference in plate shelf-life was observed.

As might be expected from the above preamble, the plates stored under high (85%) humidity conditions showed much increased loss of diazonium. This is entirely in line with what might be anticipated from the observations on coating solutions. In a typical test, when 33 % diazodiphenylamine decomposition had been measured in a conventional oven, 54 % loss occurred in the high humidity oven.

2.9.2 Negative Plates

The study of negative plate diazonium polymers in solution tests is difficult, as already described in section 2.8. These problems are made worse in the examination of negative printing plates. Although the diazonium polymer forms the bulk of the formulation, any decomposition resulted in retained polymer when the coating was extracted with solvent. This stain on the

aluminium surface was similar to the precipitate from diazonium polymer solution stability trials in that it contained a considerable proportion of intact diazo groups.

However the presence of the stain is very important for determining the shelf-life of negative plates. When negative plates are developed, the areas that have not been exposed should develop cleanly to leave a clean background. Any stain after development, resulting from diazonium decomposition, will make the background areas of the plate take ink and render the plate unsatisfactory for printing.

As the stain contained residual diazonium groups it gave an absorption on scanning its reflectance ultra-violet/visible spectrum.

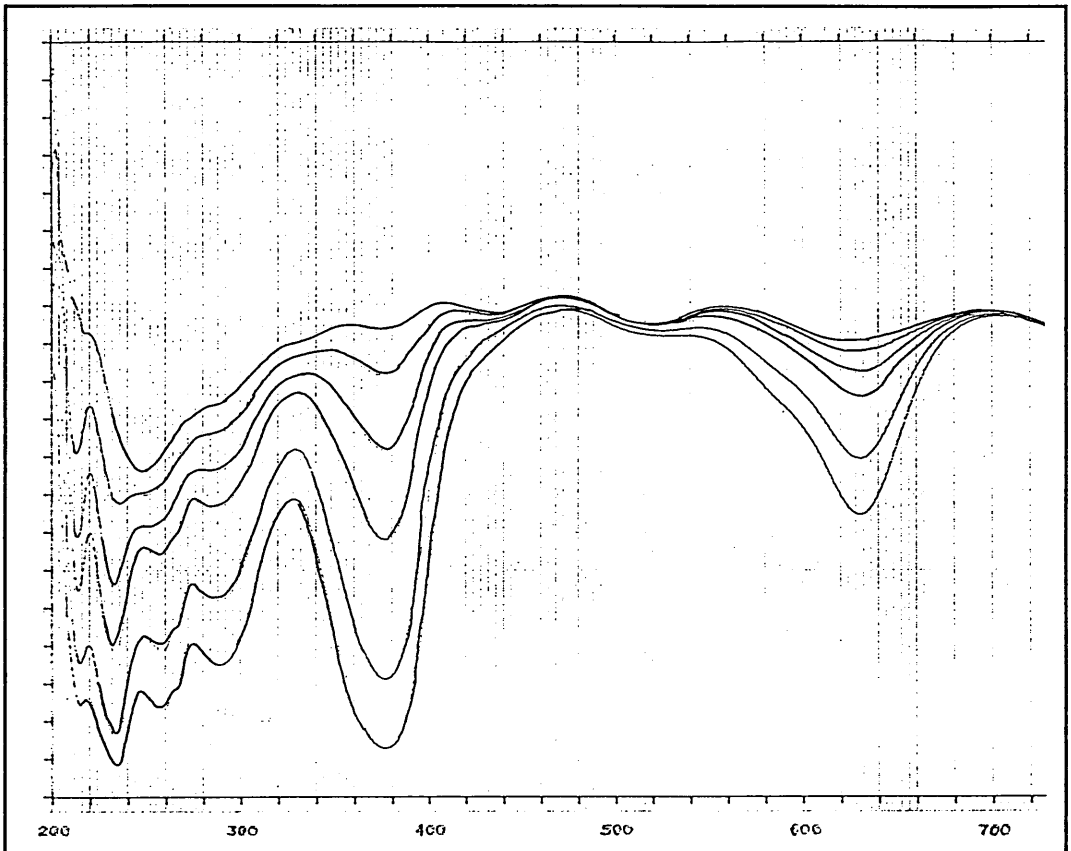


Figure 24: Superimposed reflectance UV/visible spectra during aging of a plate coated with a diazonium polymer.

This was used to give a comparative indication of the amount of decomposition that had occurred during plate

storage tests. The example above shows the diazonium stain at 380 nm from a series of superimposed plate samples.

The conclusions from this work supported those from coating solution and positive plate tests. The TFMS anion gave enhanced stability and humid storage was significantly worse than dry storage.

2.10 PHOTOLYSIS VS. THERMOLYSIS

This study of diazonium salt decomposition has been concerned with thermal decomposition and ways of limiting its effects. It is of interest to compare the processes involved in decomposition by light to see if it proceeds by a similar mechanism to thermal degradation.

Commercially, the aims are quite different. Whereas the minimum diazonium decomposition is required during the production process and during transportation to the customer, once the customer exposes the plate the quicker the diazonium groups react to the incident radiation the better.

Exposure times for positive printing plates are rapid, of the order of 30 seconds. This level of exposure was found to completely decompose diazodiphenylamine and the other diazonium salts. This contrasts markedly with the days and weeks at elevated temperature to give significant levels of decomposition by thermal means.

A direct comparison using an acetone solution of diazodiphenylamine hexafluorophosphate under a low power mercury discharge lamp gave complete decomposition in 2.5 hours. Analysis of the decomposition products gave the GC/MS total ion chromatogram below (Figure 25).

What was apparent here was the increased level of acetone decomposition products and the almost complete absence of the diphenylamine and fluorodiphenylamine observed for thermal decomposition (this would give a peak at about 2000 counts). The mass spectrum of the main product peak is given below (Figure 26).

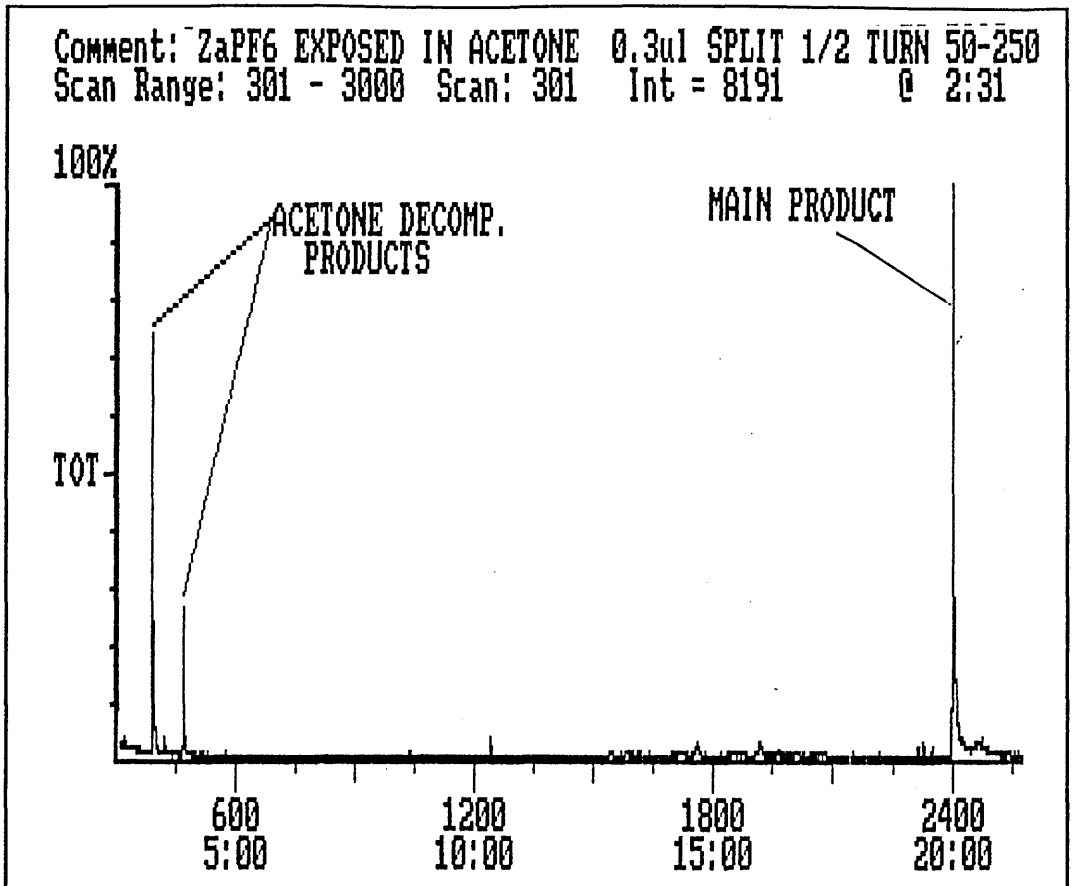


Figure 25: Chromatogram of exposed diazodiphenylamine in acetone solution after complete decomposition

The spectrum corresponds to the hydroxy substituted diphenylamine. As no water was added to the solvent and the water level was only 0.12 %, this is thought to be due to a mechanism involving decomposition of the solvent. An identical exposure in methanol gave a major peak for the methoxy substituted diphenylamine. These products indicate that a heterolytic reaction mechanism is predominating in photolysis compared to homolysis in thermal decomposition.

Further evidence for this came from GC/MS of the plate decomposition products after exposure. Whereas the major thermal decomposition product had been from hydrodediazoniation with additional higher molecular weight species from radical chain reactions, these were almost completely absent from photolysis. Instead the main decomposition product was from fluorodediazoniation.

The predominance of heterolytic reaction in the photolysis of the diazonium salts that absorb strongly at

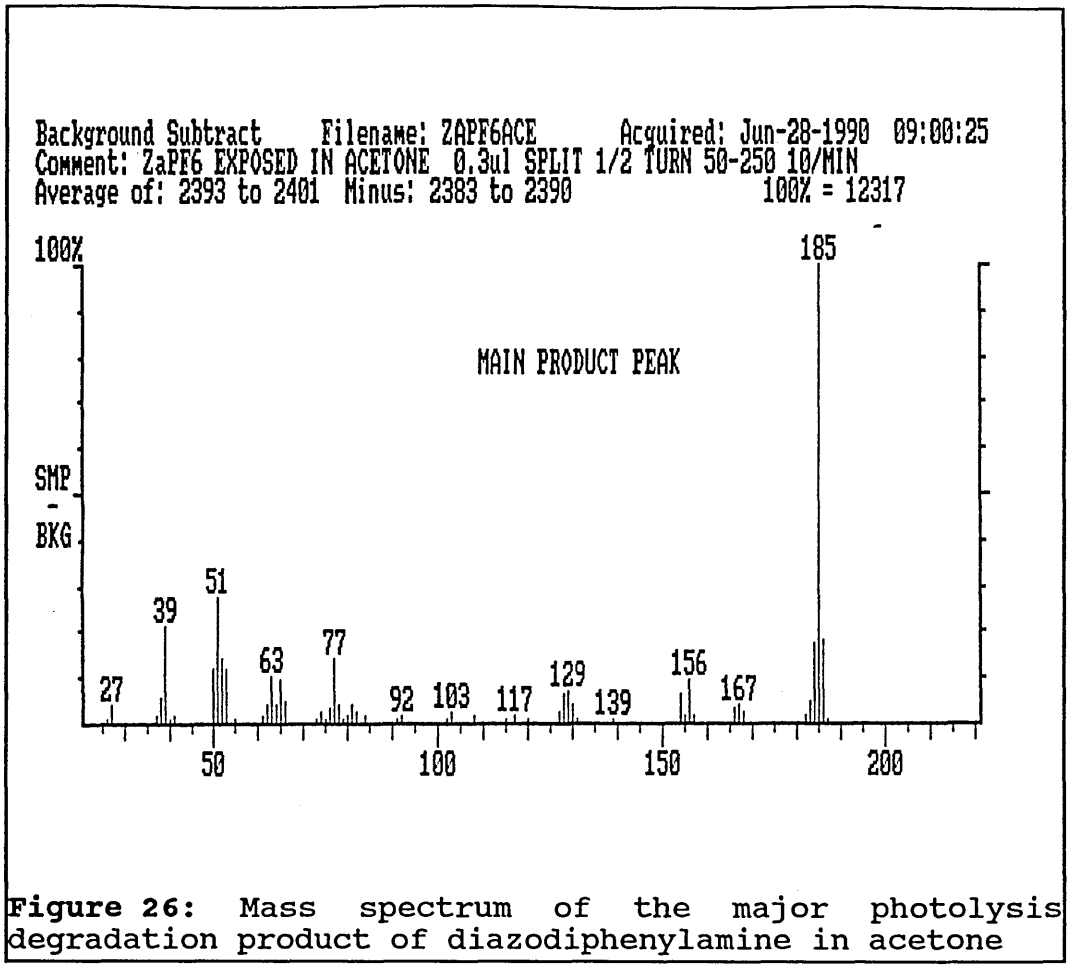


Figure 26: Mass spectrum of the major photolysis degradation product of diazodiphenylamine in acetone

longer wavelengths is a consequence of the quinoid structure that was discussed in section 1.8.4. This confers increased thermal stability while the absorption at longer wavelengths is essential for plate exposures through glass. These observations are in line with some other studies. For example increased yields of fluoro substituted products from photolysis compared to thermolysis[85] in the Balz-Schiemann reaction. Similarly the statements that " the lack of parallelism between fluoroarene yields for photolysis versus pyrolysis makes it unlikely that these reactions proceed exclusively through a common intermediate"[86] and that "the effect of electronegative substituents on the photochemical stability is inverse as compared to their effect upon thermal stability[87]" both support the differences observed. However Becker et al[30] found that in methanol, heterolytic mechanisms predominated in thermal degradation

and homolytic in photolysis. These latter may be due to the reactions in methanol being more likely to proceed via heterolytic mechanisms and that most of the diazonium compounds they investigated had electron withdrawing substituents.

As discussed in section 1.8.3 the reactions of diazonium salts proceed via a variety of mechanisms dictated by the compound itself, its matrix and now by the source of energy that instigates the decomposition.

It is worthy of note that the two required conditions for an effective diazonium compound, good thermal stability and rapid photolysis, are promoted by the same substituents. It is rare that beneficial effects are mutually supporting in this way. This fortunate reinforcement, more than any other chemical effect, has led to the development of many lithographic plate products.

2.11 CONCLUSIONS

The basis of this investigation has been to gain an understanding of the source of poor plate and plate coating thermal stability. Once this was identified as being due to poor diazonium salt stability, the factors influencing the rate of diazonium decomposition were studied in detail. Factors such as the concentration of components of the matrix (particularly cresol novolak, solvents and water), temperature and time were all found to have a major influence on the decomposition.

This information was used in conjunction with a detailed analysis of the decomposition products to identify the mechanism of decomposition as being largely due to a homolytic break in the diazonium-carbon bond via a radical process.

The identification of the decomposition mechanism led to an examination of possible means of retarding the rate of thermal degradation. Some were successful, others less

so. The factors to consider when designing an improved diazonium plate formulation are summarised in table 25.

Table 25: Factors affecting diazonium salt stability

Factor	Effect
Diazonium counterion	Electron donating ortho and para substituents give improved stability
Diazonium anion	Aromatic and short chain sulphonates give improved diazonium stability compared to BF_4^-. PF_6^- is worse, carboxylic acids give no improvement and phosphonates are very unstable.
Solvents	Affect coating solutions only. Good stabilities from low donor solvents such as acetonitrile and acetone. Poor stabilities from methanol, DMF and THF
Water	Coating solution diazonium salts affected by low levels of water. Plates also decompose more rapidly in a humid atmosphere
Novolak	Important for positive systems only. High molecular weight fractions give improved stability
Time	Depends on the matrix, temperature etc. Typically coatings decompose slowly for a few days , then rapidly over the following 10 days before slowing as concentration drops
Temperature	Depends on the matrix. Typically a small increase in rate up to 30 °C, with doubling at 40 °C and 50 °C
Concentration	Decomposition in solution accelerated at increased diazonium and novolak concentrations
Nitrogen purging	No stabilising effect
Additives	Tinuvin UV stabilisers, radical traps and theophyllines had no beneficial effect. Crown ethers, particularly 18-C-6 gave improved stability. Similar effects to 18-C-6 from high MW polyethers

3 EXPERIMENTAL DETAILS

3.1 SAFELIGHT REQUIREMENTS

All samples and standards containing diazo compounds are light sensitive and should only be handled under safe light conditions. This includes plates, plate extracts, coatings and diazo solids and solutions. Concentrated coatings and other solutions are less of a problem due to self absorption by the components reducing the harmful effects of stray light. Conversely solutions in dilute form prepared for analysis are particularly prone to rapid decomposition in just a few minutes. For this reason the work in this thesis was carried out under safelight conditions. Daylight must be excluded and either red, amber or yellow safelight used. For most of this work yellow fluorescent tube lighting provided sufficient protection.

The adequacy or otherwise of safe lighting is most easily assessed by preparing solutions of the diazo compounds to be used, and analysing their ultra-violet/visible spectra when fresh and after a time in excess of the proposed analysis time. For example, if the analysis or tests will take two hours, test the diazo compound by spectroscopy when fresh and after about three hours using methods such as 3.15. Any significant deterioration in absorption in the diazo absorption (usually in the region 360 to 420 n.m.) indicates the need for further precautions such as use of amber glassware or foil wrapping.

3.2 SOLIDS CONTENTS OF COATING SOLUTIONS

The solids content of a coating solution is measured so as to control the sensitivity of printing plates in a quality control procedure. It was measured in the work described in this thesis in order to express the measured level of coating components in terms of % w/w of coating

solids rather than as % w/v (gm per 100 ml) of coating solution. This made comparisons between plate and coating formulations easier as both were then quoted as %w/w. The solids content was determined gravimetrically.

The coating solutions for analysis were accurately diluted down by 20 times with acetone for coatings of about 10-15 % solids and proportionally for other coating concentrations to give an approximately 0.5 % w/v solution. Two aluminium dishes were accurately weighed on an analytical four place balance. 10ml aliquots of the diluted coating solution were pipetted onto each of the dishes. The dishes were placed under a hot (about 100 °C) infra red lamp in a fume cupboard. It was important to prevent igniting the solvent vapour by ensuring that the fume cupboard was switched on, and to allow a gap of about 15cm for air to flow across the dishes. The lamp was used to remove the bulk of the solvent safely before the final drying in the oven.

After 15 minutes under the I.R. lamp, the dishes were put in an oven at 105 °C for 30 minutes. Then the dishes were removed and reweighed. The difference in weights between the empty dish and the dish containing the dried down diluted coating residue gave the solids content of the 10ml aliquots of the diluted coating. From this figure (calculated as the average value of that obtained from the two dishes) the solids content of the original coating was determined. This is expressed in grammes per 100ml. of coating solution.

3.3 PLATE COATING WEIGHT

Lithographic printing plates have coating weights of 1-2g/m^2. The parameter has a direct effect on plate sensitivity; the higher the coating weight the more light is needed to give it the correct exposure. The coating weight is also used when measuring the concentration of plate components so as to give values in %w/w which can be

more easily compared with coating and other results than figures in mg/m^2.

The test was always carried out in duplicate because the weight of coating on a given area of aluminium is so small that errors due to moisture uptake from the atmosphere can significantly affect the results. Pieces of plate 10x10 cm. were cut out of the test plate. They were accurately weighed on a four place analytical balance making sure the balance doors are closed. This is about the largest size of plate that can be weighed accurately without folding. Folding the plate makes coating removal and drying inaccurate. The coating was washed off with a suitable volatile solvent such as acetone. The plates were dried off with a warm hair drier and reweighed. The difference in weight compared to the original piece of plate gave the weight of coating on 100 cm^2 of plate. This figure multiplied by 100 gave the final result in grammes per square metre.

3.4 HPLC METHOD FOR 2,1,5 NAPHTHOQUINONE DIAZO ESTER OF 2,4 DIHYDROXYBENZOPHENONE

The diazo ester structure is given in section 2.1 (16). It consists of about 80% bis and 15% mono ester with un-reacted starting materials as impurities. It is a light sensitive material and therefore cannot be analysed under normal laboratory conditions, but requires suitable safelight. This method was primarily used for coating solutions but was also adapted for plate samples after the coating was removed quantitatively with a small amount of acetone.

Typically a piece of plate 7.5x10 cm was cut into small strips to fit inside a small 12ml. capacity jar with a clip-on lid. 10 ml. acetone was pipetted into the jar which was sealed with the lid and shaken manually for a few minutes to extract the plate coating. The coating extract was then treated in the same way as the diluted coating solution below.

Coatings were diluted down quantitatively by pipetting 5 mls into a 100 ml flask and making up to the mark with acetone. The diluted solution was also used for the solids content determination (3.2), if that was required, or so as to recalculate the results in %w/w.

The method utilised a High Performance Liquid Chromatograph (HPLC) to separate the diazo ester mono and bis components from each other and any other coating components. Both the dye and diazodiphenylamine acid release were found to interfere with attempts to develop a method of analysis based on ultra-violet spectroscopy (UV) alone.

The equipment used was a modular system incorporating a Kontron 460 auto-injector, Waters 510 pump, Waters 490 UV detector and either a Spectra-Physics SP4270 or Trivector Trio data handling system. A Rheodyne injector 7125 with a fixed loop was used occasionally and worked equally well. An eluent of 50:50 tetrahydrofuran (using stabilised THF from May & Baker) and distilled water was used . This was pumped at 2 ml/min. A guard column and analytical column were used in series. The guard column was a manually packed 2 cm. column containing 37-50 micron C18 reverse phase packing based on a silica support. The analytical column was a Waters Novopak 4 micron C18 reverse phase packing in a radial compression column holder (RCM 200). This holder maintained sufficient pressure around the column to eliminate the formation of voids in the packing material which would otherwise have led to a loss of chromatographic efficiency.

The UV detector was set at 365 n.m. and 0.5 A.U.F.S. (0.2 A.U.F.S. for plate extracts). 20 microlitres of sample was injected and the diazo ester components eluted after about 4 minutes for the bis ester and 5 minutes for the mono ester. The dye eluted on the solvent front and the diazodiphenylamine was retained under these conditions.

Quantification was by measuring the peak areas and calculating the mono and bis diazo ester levels separately

with reference to a diazo ester standard. The standard used was a secondary one which is a sample obtained from International Biosynthetics (Hale Cheshire) . This contained a similar mixture of mono and bis esters and was in turn calibrated by HPLC against primary purified standards prepared from it (see below).

About 15-20 mg. of the secondary standard was accurately weighed on a Sartorius 4401 microbalance and transferred to a clean dry 50 ml. graduated flask. Stabilised THF was added to the mark. Duplicate standards were used and the area/concentration factors averaged. Duplicates were usually in agreement to 2%. It was essential to closely match the concentrations of the standards to the diluted coatings or plate extracts. The sample response was bracketed between those of the standards. This was to reduce any errors due to none linearity of response or column overloading. Duplicate samples were also carried out and the final quoted result is the average of the duplicates.

Primary Standard Preparation

The primary standards were prepared from about 3 gms. of a diazo ester batch which had a fairly high mono content of about 18%. 25 mls. of ethyl acetate was pipetted onto the sample contained in a beaker. The sample slurry was put in a sonic bath for 10 minutes. Then removed and allowed to stand for an hour when some precipitation occurred. The solid was centrifuged off to give a relatively bis rich residue, the liquors being relatively rich in mono ester.

The liquors from the above process were evaporated down to dryness in a vacuum oven at ambient temperature, and the solids run down a silica preparative column using 90:10 chloroform : MEK, collecting the mono fraction only. This was dried down and the process repeated. This yielded about 80% pure mono ester. This was purified further using reverse phase HPLC with a fraction collector to collect

the mono fraction. Evaporation of the mono containing fractions on a rotary evaporator left a fine suspension of mono ester in water which was centrifuged off and dried in a vacuum oven overnight at 30 °C. This resulted in about 50 mgs. of the primary mono standard whose purity was verified by only getting a single peak on HPLC analysis corresponding to the known position of the mono component, and by elemental analysis.

The bis rich fraction was run down a gravity fed open column packed with silica gel using an eluent of 90:10 chloroform : MEK collecting the major fraction that eluted after the mono ester. It was necessary to use thin layer chromatography periodically to check which fractions contained the bis ester. The solution of the diazo ester were dried down in a rotary evaporator and then put down a second column. The solution was dried and washed with n-hexane before drying in a vacuum oven at ambient. This process resulted in about a gramme of primary bis ester standard and its purity was verified in the same way as for the mono standard above, by HPLC and elemental analysis.

Both the primary and secondary standards were stored in a refrigerator where they remained stable over a period of 2 years.

3.5 HPLC METHOD FOR COLOUR CHANGE DYES IN COATINGS

This method used the same equipment and columns as given in method 3.4. A weaker eluent of 40:60 stabilised THF: water was used to give sufficient retention to resolve the dye from the solvent front. The method was applicable to various dyes of generalised structure (18). When used for the analysis of coatings of plate extracts the same dilutions of sample are used as for diazo ester in method 3.4. The UV detector was set to 405 nm. 0.2 A.U.F.S. for coatings and 0.1 A.U.F.S. for plate extracts. The eluent was pumped at 2 ml./min. The dye eluted after about 3-4 minutes. Diazo ester eluted after about 12

minutes but the diazodiphenylamine did not elute under these conditions. 20 microlitres of sample and standard were injected. The standard was a purified version of a batch of the dye which was itself prepared at DuPont Howson. It was purified for use as a standard by dissolving about 5 gms. of the dye in about 100 ml. of a 2:1 ethanol:water mixture. The solution was filtered to remove any insoluble material and the liquors allowed to cool slowly in petri dishes. The dye crystallised out on standing. The crystals were filtered off and the procedure repeated with a further 100ml of ethanol : water mixture. Finally the solid was filtered off and dried overnight in a vacuum oven at 40 °C.

Standards and samples were analysed in duplicate and the final quoted results were averages of duplicates that were in agreement to 5 %.

3.6 HPLC ANALYSIS OF DIAZODIPHENYLAMINE SALTS

Diazodiphenylamine with counterions such as, for example, the tetrafluoroborate (17) or hexafluorophosphate presented a difficult sample for analysis. Not only was it very unstable both thermally and photochemically, but as a salt it presented problems for HPLC analysis. The column packing used was a reverse phase packing that was fully end capped to reduce the presence of residual reactive silanol groups. Nevertheless the diazonium salt was sufficiently reactive that rather than eluting on the solvent front, as might be expected of a salt in a water/solvent mixture, it was completely retained unless buffer and salt additions were made to the eluent to deactivate the column.

The use of ion-pairing reagents such as heptane-sulphonic acid (0.005 M), with acetic acid added to adjust the pH, gave elution in a reasonable time. However this was as a broad tailing peak which could only be improved by the use of excessive quantities of this reagent. Much better was the use of sodium lauryl sulphate/acetic acid

mixture which was used to give elution as a sharper peak, and is a cheaper reagent. The mechanism for the elution is thought to be a combination of deactivation of the column (with the lauryl sulphonate groups masking any reactive sites), and ion-pairing.

The HPLC equipment and columns were as in method 3.4. The eluent was prepared by dissolving 18.5 gms. of sodium lauryl sulphate in a litre of distilled water containing 20 ml. glacial acetic acid. To this was added one litre of Analar acetone. This was thoroughly mixed and filtered through a 0.45 micron filter under vacuum.

The eluent was used at 2 ml./min. with the U.V. detector set at 405 nm. and 0.5 A.U.F.S. Injections of 20 microlitres of both samples and standard were used. Coating samples required diluting 5 ml to 100 ml acetone. Plate extracts were prepared as in 3.4 and analysed at 0.1 A.U.F.S.

Under these conditions the diazodiphenylamine eluted after about 5 minutes. Any colour change dye that also absorbed at 405 n.m. was on the solvent front. The diazo ester eluted at about the same position as in method 3.4, with the bis ester at 4 minutes and the mono ester at 6 minutes. It was sometimes feasible to use this method for quantification of both the mono and bis diazo ester, as well as the diazodiphenylamine salt. More frequently the mono diazo ester and diazodiphenylamine salt interfered with one another depending on the condition of the column. It was therefore more practical to use method 3.4 for the mono and bis quantifications as there was then no interference from the diazodiphenylamine salt. If interference was a problem during diazodiphenylamine quantification it could usually be eliminated by small (100 ml.) additions of 50/50 acetone/water. This had the effect of making the diazodiphenylamine salt elute earlier (due to reduced ion-pairing) relative to the mono ester.

Standard commercial samples were used as standards for the quantification (eg. from A.B.M. Chemicals). 12 to 15 mg. of the diazodiphenylamine salt standard was

accurately weighed using a microbalance into a 100 ml. graduated flask and made up to the mark with Analar acetone. The solid standard was stored in a refrigerator at 5 °C. Solution standards were prepared fresh each half day.

3.7 WATER CONTENTS BY KARL FISCHER (INCLUDING KETONES)

Water contents in general were carried out by titration with Karl Fischer reagent. This well established method is based on the following reaction scheme (28)

$$CH_3OH + SO_2 + RN \rightarrow [RNH]SO_3CH_3$$

$$H_2O + I_2 + [RNH]SO_3CH_3 + 2RN \rightarrow [RNH]SO_4CH_3 + 2[RNH]I$$

(where RN = base)

(Scheme 28: Karl Fischer reaction)

The sulphur dioxide reacts with the alcohol to form an ester which is neutralized by the base. The anion of the methyl sulphurous acid is the reactive component and is already present in Karl Fischer reagent. The titration of water constitutes the oxidation of the methyl-sulphite anion by the iodine. The reaction consumes water[88].

The measurement used a Mettler Karl Fischer attachment on a DL40 Mettler titrimeter. The endpoint was detected amperometrically by twin platinum electrodes. Once there was an excess of iodine present and the water has been consumed, the endpoint was registered. Sodium tartrate dihydrate was used as standard.

Both aldehydes and ketones used to be problem groups for Karl Fischer titration as they form acetals and ketals respectively with previously used conventional reagents. Water is formed during the reaction (29) which is also titrated, resulting in erroneously high endpoints.

$$(R)_2C{=}O \;+\; 2CH_3OH \;\rightarrow\; R_2C(OCH_3)_2 \;+\; H_2O$$

(Scheme 29: Reaction of ketones to give water)

The reactivity of aliphatic ketones decreases with increasing chain length. Aldehydes are much more reactive than ketones. The formation of acetals and ketals can be suppressed by replacing the methanol in the titrating agent with another solvent. The use of pyridine and 2-methoxyethanol have been recommended for this but give low results in the case of pyridine and high results in the case of 2-methoxyethanol. Halogenated alcohols like 2-chloroethanol or trifluoroethanol have been found to give good results[89].

The proprietary reagents Hydranal (Riedel-de-Haen) for general water contents of liquids and solids and Hydranal K (specially formulated in the halogenated solvents mentioned above) were used for samples known to contain significant quantities of ketones or aldehydes. For the work described in this thesis, the major class of samples analysed for water content that contained ketones was of course coating solutions prepared in acetone. The amount of sample taken for the analysis was found empirically and varying amounts were taken depending on the water content, until a suitable titre was obtained.

3.8 HEXAFLUOROPHOSPHATE AND TETRAFLUOROBORATE BY ION CHROMATOGRAPHY

Ion chromatography (IC) in its original configuration[90] was a form of high performance liquid chromatography that utilised a stationary phase of ion-exchange resin and conductivity detection. Using a low capacity anion exchange column and an eluent based on sodium carbonate/bicarbonate mixtures it was possible to separate most common anions in about 20 minutes with baseline resolution.

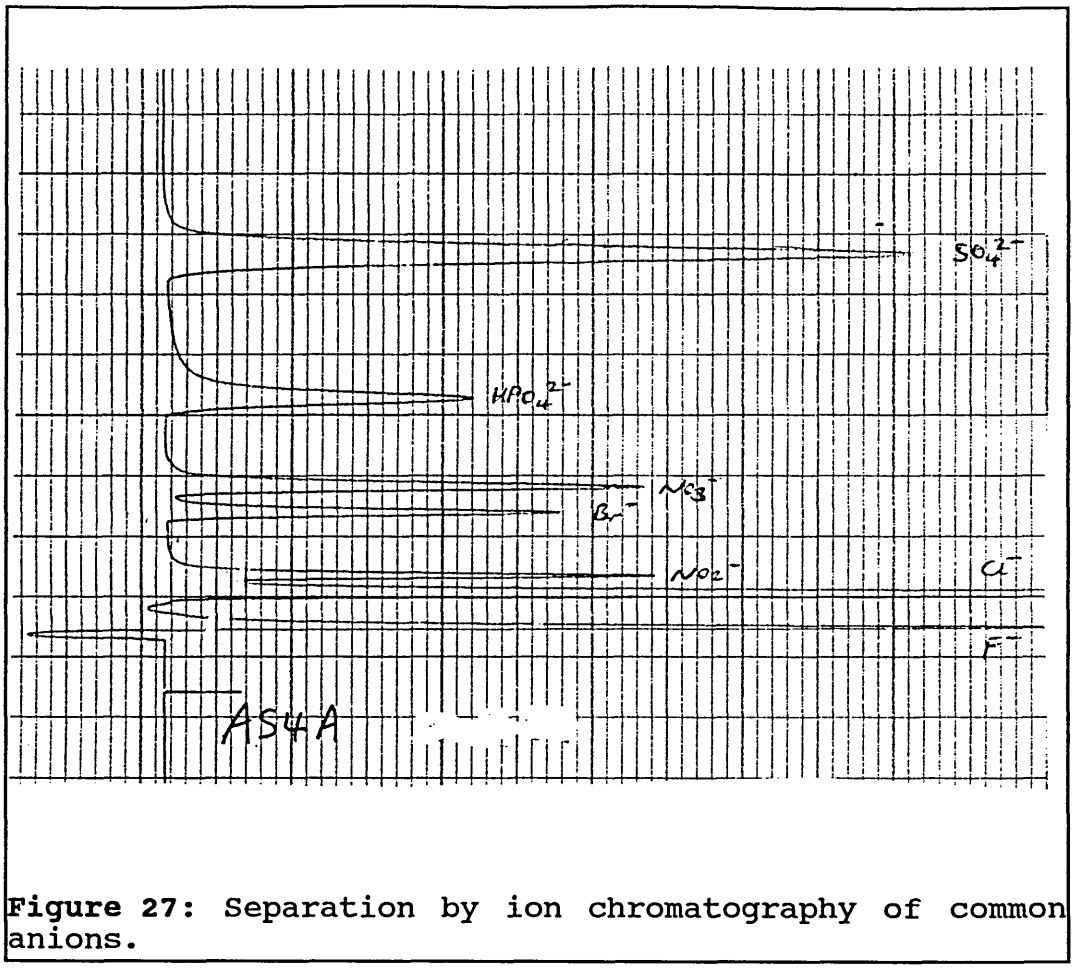


Figure 27: Separation by ion chromatography of common anions.

The major innovation that Small and coworkers patented related to the suppression of the conductivity of the eluent. They used a second column in series with the first, that possessed a cation exchange functionality. This replaced the sodium in the eluent with protons to convert from fully ionised sodium salts to weakly ionised carbonic acid. More sophisticated and improved versions of this initial idea became incorporated in the new ion chromatographs. The most recent utilise an anion micro membrane suppressor (AMMS) which is shown diagrammatically below (Figure 28).

This works in the same way as the cation exchange suppressors, but has a flow of weak sulphuric acid around the membrane that continuously regenerates the ion exchange capacity.

Although some of the initial measurements of tetrafluoroborate were carried out using the anion

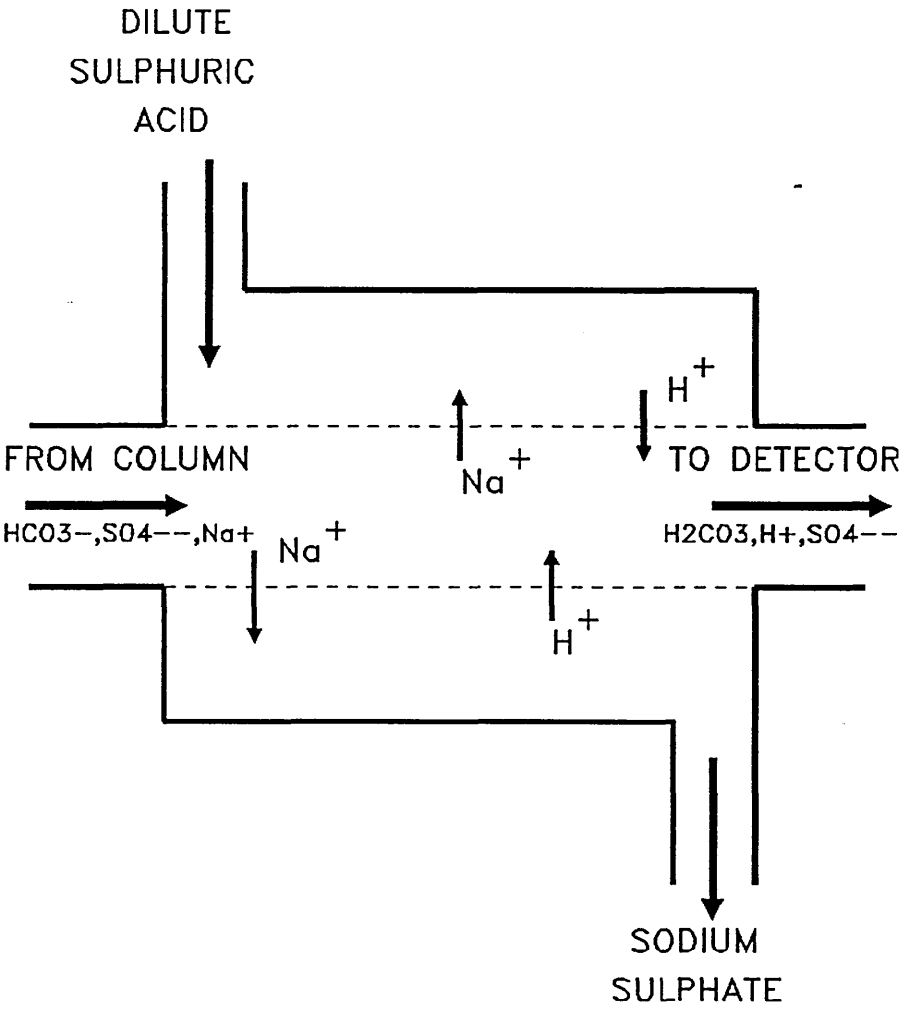


Figure 28: Ion chromatography anion micro-membrane suppressor.

separator column and the AMMS suppressor with sodium carbonate based eluents, the peak eluted late and tailed badly. This made quantification inaccurate and time consuming. In addition, when an attempt was made to quantify the hexafluorophosphate anion, no peak could be detected under these conditions.

Recent developments in column technology by Dionex and others have meant that the dividing line between conventional HPLC and IC have become even more blurred than when the technique was patented. This is not only in the use of column packings, but the eluents and detectors used are often those associated with conventional HPLC. It is quite common to use solvent/water eluents and UV

detection as in HPLC. However, the strength of the original technique is as applied to anions. One method of analysing these by reverse phase HPLC is to utilise ion-pair reagents. These reagents are usually long chain ions of the opposite charge to that of the analyte. For example, heptane sulphonic acid is used to ion-pair with cations and tetrabutyl ammonium hydroxide is used for anions; buffered to pH 8 or below to prevent damage to silica based column packings . The ion-pairing converts the analyte ion into an overall non-polar species which can be retained by reverse phase HPLC packing materials.

In the case of the complex anions under investigation, this method was adopted but conductivity detection was used as neither of the anions has appreciable UV response. A neutral resin based on polystyrene was the stationary phase. This had the advantage of being useable at high pH which is a problem with HPLC packings based on oleophilic species bonded to silica.

The final conditions were using a Dionex 4000i IC with a MPIC separator column and guard column in series with an AMMS suppressor. A flow rate of 1 ml/min. was used with an eluent containing 2mM tetrabutylammonium hydroxide in either 30:70 acetonitrile:water for BF_4^- or 50:50 acetonitrile:water for PF_6^-.

3.9 GAS CHROMATOGRAPHY / MASS SPECTROMETRY OF POSITIVE PLATE COMPONENTS

For very sensitive analysis of low levels of decomposition products formed on heating positive plates a gas chromatograph (GC) linked to a mass spectrometer (MS) was used. The GC was a Perkin Elmer model 8500 with a heated transfer line to the MS which was a low resolution ion trap spectrometer, the Finnegan ITD.

Test plates were prepared by whirling about 20 ml. of a positive coating formulation onto a 30 x 30 cm.piece of plate as detailed in 3.10. For tests on thermally

decomposed plates, the plate was stored at 105 °C for 24 hours in an oven. A sample of plate 5 x 10 cm. was cut up into small pieces to fit inside a 10 ml. sample bottle. 2ml Analar acetone was added and the bottle sealed and shaken for a few minutes to extract the plate coating. 0.5 microlitres of the extract was injected into the GC where it underwent a 10:1 split before being separated on a DB5 capillary column. This column is a 5% phenyl, 95% methyl stationary phase present as a 0.1 micron film. The column was 30 metres long with an internal diameter of 0.25 mm.

The GC oven was programmed to be held at 50 °C for 2 minutes, then to rise at 10 °C per minute to 250 °C where it was held for a further 2 minutes. The helium carrier gas was ultra pure and set to an inlet pressure of 23 psi (1 ml/minute).

The ITD was set up at a multiplier voltage of 1650 volts and an overall temperature of 250 °C. This temperature set the oven splitter temperature to 250 °C, the transfer line to 245 °C, the nozzle into the trap at 258 °C and the manifold temperature to 242 °C. The mass range scanned was 45 to 650 Daltons with a scan time of 0.5 seconds during which 2 microscans were taken. A calibration was carried out against an instrument resident calibration compound. Atomic masses 28,29,32 and 44 were tuned out to eliminate overloading the detector with possible atmospheric contaminant gases ie. nitrogen (28,29), oxygen (32) and carbon dioxide (44). These can sometimes cause problems with the detector if they are not screened out, due to the high vacuum it is operating under.

With these conditions the diazodiphenylamine decomposition products had a retention time of about 16 minutes.

Thermal Desorption

For even greater sensitivity, some work was carried out at Luton College using the same GC/MS combination as

above but with automatic thermal desorption of the sample plate into the GC. All the volatiles from the piece of plate entered the GC rather than only 0.5 microlitres of an acetone extract as above. The desorber instrument was a Perkin Elmer ATD 50. The same column size and stationary phase was used as before but with a 150:1 split ratio from the thermal desorber.

The ATD 50 uses stainless steel tubes 9 cm. long with an internal diameter of 5 mm. A strip was cut off the test plate 2mm. by 3cm. and put in the sample tube, supported by a stainless steel gauze. The tube was heated to 250 °C for 8 minutes to drive off any volatiles; including residual coating solvent, cresols and diazodiphenylamine salt decomposition products. These were trapped in a cold trap containing Tenax packing at -30 °C. When the desorption time had elapsed, the cold trap was "fired" which entailed rapidly heating it to 275 °C. This stripped off the volatiles as a concentrated "slug" to give a sharp band of components on the head of the GC column. Transfer from the desorber to the GC was via a fused silica insulated heated transfer line. The GC oven was programmed to ramp up the temperature from an initial period of 3 minutes at 50 °C, to 250 °C at a rate of 10 °C per minute, holding at 250 °C for 5 minutes. The helium carrier gas was at an inlet pressure of 18 p.s.i. Under these conditions the diazodiphenylamine decomposition products had a retention time of about 20 minutes.

3.10 PREPARATION OF EXPERIMENTAL TEST PLATES

Plates were prepared for experimental work using a whirler. This is a rotating disc about a metre in diameter that can be rotated in a horizontal plane at a preset number of revolutions per minute. The rotating disc is housed in a tank that has extraction to remove solvent vapour. The grained and anodised aluminium substrate was clamped to the centre of the disc. Usually a piece about 30 x 30 cm. was used. The coating had to be fairly dilute

to be of low enough viscosity to give an even coating. Typically a solids content of about 5% w/v (gm per 100ml) in a volatile solvent such as acetone gave good results. The disc was set up rotating at 120 r.p.m. About 10 to 15 ml. of the coating solution was poured steadily onto the rotating disc. The spinning disc spread the coating out in an even film across the aluminium substrate. After the coating had been added, the disc was left to rotate with the tank lid down and extraction on for about 5 minutes to drive off the bulk of the solvent. The plate was then removed from the whirler and dried with a warm hair drier. Finally, if it was necessary to simulate commercial plate production as closely as possible, the plate was placed in an oven at 100 °C for 5 minutes.

This technique needed some practice to give an even coating with a coating weight in different parts of the plate within the normal commercial plate tolerances.

3.11 GEL PERMEATION CHROMATOGRAPHY

The use of high performance liquid chromatography (HPLC), has become widely used to quantify monomeric species in liquids. It finds extensive application for the analysis of components not volatile enough to be analysed by gas chromatography. The same HPLC equipment can also provide information on polymeric components in sample matrices. This technique is Gel Permeation Chromatography (GPC). By comparison with polymers of known molecular weight, the molecular weight of sample polymers can be established in a short time, usually less than 20 minutes. Conventional HPLC utilises the differing partition of sample components between the mobile phase and the stationary phase to achieve a separation of the components. The mobile phase is usually a mixture of organic solvent and water with use of buffer salts to optimise the separation and peak shape. The stationary phase is typically a hydrophobic resin with long chain C18 functionality. However in GPC a mobile phase of organic

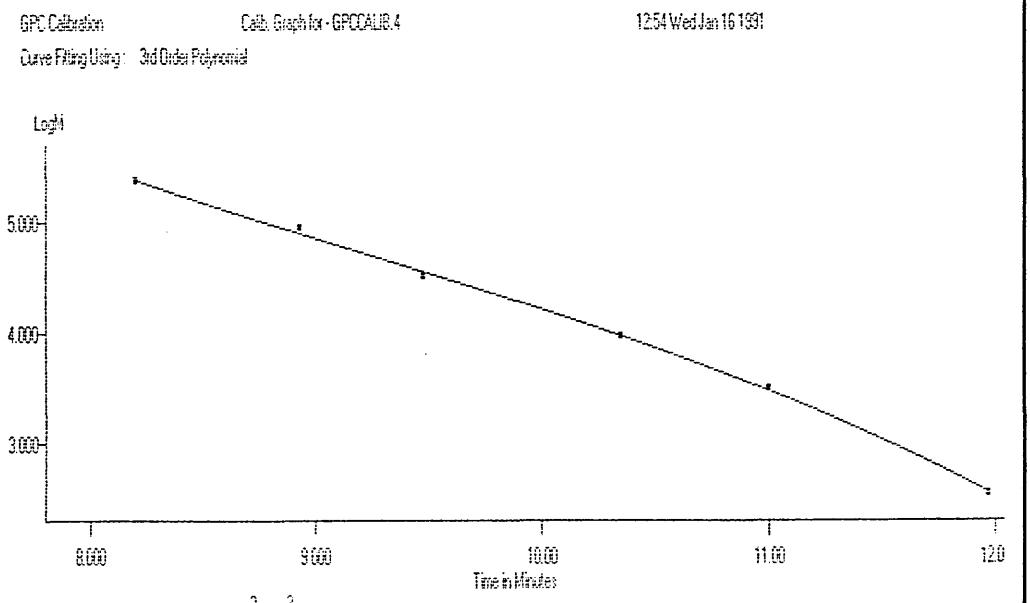
solvent only is used with a stationary phase of a styrene divinyl benzene or other inert material.

Separation occurs not according to chemical affinity for either the mobile or stationary phase, but rather according to the varying size and shape in solution of polymer molecules. Ideally separation should be entirely due to the physical size differences and the column packing should be inert. The packing material achieves the separation by means of small pores within the packing particles. Polymer molecules small enough to enter the pores spend some time out of the flowing solvent stream which flows around the packing particles. This results in larger molecules, that are unable to enter the pores, remaining in the faster flowing solvent stream and eluting first from the column.

In this investigation, GPC was used to separate novolak fractions using a mobile phase of tetrahydrofuran (THF). A column system was used that incorporated a range of pore sizes in a single column. Two columns were used in series to give adequate resolution. The columns used were mixed bed PLgel columns from Polymer Laboratories containing styrene divinyl benzene copolymer. Novolak samples at a concentration of 0.2 gm in 10 ml THF were injected from a 20 microlitre Rheodyne injector into the THF mobile phase at a flowrate of 1.5 ml/minute. The polymer fractions eluted at between 8 and 14 minutes to give broad molecular weight distributions. Detection in GPC is traditionally by refractive index but for polymers with a strong ultra-violet absorption, as in this case, spectroscopic detection is preferred. A UV detector was used as outlined in methods relating to HPLC in this section. The detector was set to 254 nm. and an attenuation of 0.2 AUFS.

The calibration was carried out using polystyrene calibration standards of low polydispersity from Polymer Laboratories. Low polydispersity is essential if the retention times are to be assigned to a single molecular weight in the calibration graph. Polydispersities were

between 1.00 and 1.16 for all the standards. On injection both the polymer standards and the samples incorporated an internal retention marker of toluene. This was used to correct retention times for any slight fluctuations in pump flowrate. This precaution is essential in GPC work given the logarithmic relationship between molecular weight and retention time. The log molecular weights of the standards were plotted against retention time using a Polymer Laboratories data station with a third order polynomial calibration that closely simulates the theoretical relationship between the two parameters. The results are shown in Figure 29.



Point	Name	RT(mins)	MolWt	LogM	Fit Ratio	Used
1		8.20	250000	5.371	0.959	Yes
2		8.93	89000	4.949	1.010	Yes
3		9.48	32500	4.512	0.991	Yes
4		10.35	9350	3.964	0.939	Yes
5		11.00	3100	3.491	1.006	Yes
6		11.97	350	2.544	0.956	Yes

Figure 29: Gel permeation chromatography calibration using polystyrene molecular weight standards, corrected using a toluene retention marker.

Polymers whose profile extends beyond the calibration limits will be measured against an extrapolation of the third order polynomial relationship. This will result in

relatively little error for lower molecular weights, but will give a significant error for higher molecular weights (as is the case for one of the fractions in this investigation). This is not usually a major drawback as GPC is used for rapid comparative results. Other calibration standards can be used to extend the range if greater accuracy is required. The other difficulty with GPC, if absolute molecular weights are required, is the different relationship between hydrodynamic volume for the calibrant molecules compared to those of the analyte. This difference can be overcome either by making fractions of low polydispersity and free of monomeric contaminants from polymer of similar composition to the analyte, or by correcting for the difference in molecular weight/retention time relationship using viscosity data.

3.12 INFRA-RED SPECTROSCOPY

The infra-red spectrophotometer used was a Fourier Transform (FT) Mattson Polaris with an MCT detector and a water cooled source. The detector was cooled with liquid nitrogen. Solid samples were analysed as KBr discs. Liquid samples, such as stability test solutions, were measured as undiluted samples in a fixed path length cell. A typical path length was 0.1 mm. Data handling was carried out on a Tandon computer, utilising Icon software.

3.13 THERMAL ANALYSIS

Thermal analysis was carried out using a Mettler DSC 30 Differential Scanning Calorimeter. Samples of between 2 and 5 milligrammes were weighed out on a microbalance. The samples were scanned over a range of 30 to 300 °C at a heating rate of 10 °C/min. Air was used as a purge gas at a flow rate of 50 ml./min. The onset of decomposition, the maximum temperature of the exotherm and the energy evolved were measured from each sample analysis.

3.14 HYDROXY VALUE OF NOVOLAKS

The hydroxy value of novolaks and cresol were measured using a method adapted from "Organic Analysis via Functional Groups"[91]. The sample solution was reacted with an excess of 1 M acetic anhydride with perchloric acid present. The excess anhydride was hydrolysed to the acid and titrated with 0.55 M potassium hydroxide using thymol blue indicator.

3.15 ULTRA-VIOLET/VISIBLE SPECTROSCOPY OF DIAZONIUM SALTS

Many of the diazonium salt stability solutions were measured by ultra-violet/visible spectroscopy (UV/vis). This was an accurate method for a range of diazonium compounds that were strongly coloured and had absorption maxima (λ max.) in the range 350-410 nm. A Lambda 5 Perkin-Elmer spectrophotometer was used for the measurements. It was set to the λ max. for the diazonium salt under investigation (found by a wavelength scan of the diazonium salt only in acetone). Full coating solutions containing dyes and diazo ester could not be analysed by this technique, but simpler solutions with just the diazonium salt, cresol or cresol novolak in a solvent could use this method.

Stability solutions with typically 10 % w/v novolak and 0.25 % diazonium salt were diluted down quantitatively 100x with acetone and their absorptions measured at the λ max. The concentration could be measured by analysing standards of known concentration or the decomposition measured as a percentage of the absorption of the fresh stability solution.

3.16 PULSED SQUARE WAVE VOLTAMETRY

Equipment at Sheffield City Polytechnic was used for the pulsed square wave voltametry study of diazonium salts. The instrument was linked to an Amstrad computer

for data handling and a printer. Solutions were prepared at a strength of 1 millimolar in acetonitrile. About 50 ml. of this solution was mixed with an equal volume of tetrabutylammonium phosphate buffer which was at a strength of 0.1 M in acetonitrile. The solution was purged with a nitrogen stream for a two minutes, partially sealed with plastic film and scanned from 1 volt to -1 volt. Initially a carbon electrode was used, but no reduction was detected. Good results were obtained using a gold electrode provided its surface was renewed by slicing off the end few millimetres after every four sample runs.

A blank solution of diluted buffer was also analysed to ensure any reduction detected was due to the sample and not the matrix.

3.17 ION-EXCHANGE OF THE DIAZONIUM COUNTERION

The exchange of the diazodiphenylamine anion to give a range of alternatives was carried out following the development of a general method that was subject to minor variations to give good ion exchanged product. One method could not be universally applied because of the widely varying solubility of the anionic species before and after ion exchange.

The general method was based on preparing a 1gm./50 ml. solution of diazodiphenylamine bisulphate salt in distilled water. This was added slowly with stirring to a 1gm./50 ml. distilled water solution of the new counterion present as either the acid or sodium/potassium salt in a small beaker. If the new anion solution was partially insoluble, a small amount of acetone was added to help it to dissolve. The diazonium bisulphate was added to the counterion solution so as to make ion exchange more likely due to the large initial excess of counterion.

The solution and any ion exchanged precipitate were extracted three times with 30 ml. portions of chloroform. It was possible to check if the diazonium salt had ion exchanged by observing the colour of the chloroform

extract in white light. If the extract was yellow, ion exchange had occurred to give a solvent soluble product.

The combined extracts were in turn extracted with 50 ml. water. Finally the washed chloroform solution was rotary evaporated to near dryness and drying completed using a vacuum oven at 40 °C. The ion exchanged diazonium solutions were checked for purity by elemental analysis.

4 REFERENCES

1. P. Griess Annalen der Chemie 1858, 106, 124
2. P. Griess J.C.S. 1867, 20, 36
3. E. Bamberger Berichte der Deutschen Chemischen Ges. 1895, 28, 538
4. J. B. Polya Chem. Ind. (London) 1965, 812
5. L. Bersier, L. Valpiana, H. Zubler Chem.-Ing.-Tech. 1971, 43, 1311
6. L. Wolff Liebigs Ann. Chem. 1900, 312, 125
7. O. Sus Liebigs Ann. Chem. 1944, 556, 65
8. O. Sus Liebigs Ann. Chem. 1947, 557, 237
9. O. Sus Liebigs Ann. Chem. 1953, 579, 133
10. K. P. Zeller J.Chem. Soc., Chem. Commun. 1975, 317
11. J. March "Advanced Organic Chemistry" J. Wiley & Sons 1985, 602
12. J. Furakawa, T. Saegusa "Polymerisation of aldehydes and oxides" Interscience, Wiley, New York 1963, 129
13. A. Roe Org. React. 1949, 5, 193
14. R. J. W. Cremlyn and R. H. Still "Named and Miscellaneous reactions in Practical Organic Chemistry" Heinemann 1967, 3
15. H. G. O. Becker and G. Israel J. Prakt. Chem. 1979, 321, 579
16. C. G. Swain, R. J. Rogers J. A. C. S. 1975, 97, 799
17. K. G. Rutherford, W. Redmund, J. Rigamonti J. Org. Chem. 1962, 26, 5149
18. W. Salomon, U. Roth Patent Ger (East) 1986, DD236,518
19. A. Mueller, U. Roth, S. Siegert, R. Mietchen Z. Chem. 1986, 26, 169
20. M. J. S. Dewar "The Electronic Theory of Organic Chemistry" Oxford University Press 1949, 1820
21. C. Romming Acta Chem. Scand. 1959, 13, 1260 and 1963, 17, 1444
22. M. Sukigara and S. Kikuchi Bull. Chem. Soc. Japan 1967, 40, 461
23. I. A. Koppel and V A. Pal'm Reakts. Sposobnost Org. Soedin. 1971, 8, 291

24. L. C. Anderson and J. W. Steedly Jr. J. A. C. S. 1954, 76, 5144
25. M. Aroney, R. J. W. Le Fevre and R. L. Werner J. Chem. Soc. 1955, 276
26. K. B. Whetsel, G. F. Hawkins and F. E. Johnson J. A. C. S. 1956, 78, 3360
27. R. H. Nutall, E. R. Roberts and D. W. A. Sharp Spectrochim. Acta. 1961, 17, 947
28. J. F. Bunnett J. Chem. Soc. 1954, 4717
29. H. Zollinger Angew. Chem., Int. Ed. Engl. 1978, 17, 141
30. H. G. O. Becker,E. Fanghanel and K. Schiller Wiss. Z. Tech. Hochsch Chem. Leuna-Merseburg 1974, 16, 322
31. M. L. Crossley, R. H. Kenle and C. H. Benbrook J. A. C. S. 1940, 62, 1400
32. E. S. Lewis and J. M. Insole J. A. C. S. 1964,86, 34
33. C. G. Swain and E. C. Lupton Jr. J. A. C. S. 1968, 90, 4328
34. R. G. Bergstrom, R. G. M. Landells, G. H. Wahl Jr. and H. Zollinger J. A. C. S. 1976, 98, 3301
35. Y. Hashida, R. G. M. Landells, G. E. Lewis, I. Szele and H. Zollinger J. A. C. S. 1978, 100, 2816
36. T. J. Broxton, J. F. Bunnett and C. H. Paik Chem. Commun. 1970, 1363
37. J. F. Bunnett and H. Takayama J. Org. Chem. 1968, 33, 1924
38. C. D. Johnson "The Hammett Equation" Cambridge University Press 1973
39. J. Hine "Structural Effects on Equilibrium in Organic Chemistry" Chapt. 3, Wiley Interscience 1975
40. E.S. Lewis and M. D. Johnson J. A. C. S. 1959, 81, 2070
41. C. G. Swain, J. E. Sheats and K. G. Harbison J. A. C. S. 1975, 97, 783
42. R. A. Bartsch and P. Carsky J. Org. Chem. 1980, 45, 4782
43. P. Burri and H. Zollinger Helv. Chim. Acta. 1973, 56, 2204

44. P. Burri, H. Loewenschuss, H. Zollinger and G. K. Zwolinski Helv. Chim. Acta. 1974, 57, 395
45. J. Besse and H. Zollinger Helv. Chim. Acta. 1981, 64, 529
46. V. Gutmann Electrochim. Acta. 1976, 21, 661.
47. A. Freer Bull. Soc. Ind. Mulhouse 1891, 61, 220
48. A. Mostad and C. Romming Acta. Chem. Scand. 1968, 22, 1259
49. W. Lange and E. Muller Ber. 1930, 63, 1067
50. P. Becker D.R.P. patent 81039
51. Z. A. Veinberg Anilinokras. Prom. 1934, 4, 281
52. G. J. Marriott J. S. D. C. 1936, 52, 172
53. E. P. Kyba, R. C. Helgeson, K. Madan, G. W. Gokel, T. L. Tarnowski, S. S. Moore and D. J. Cram J. A. C. S. 1977, 99, 2564
54. G. W. Gokel and D. J. Cram J. C. S. Chem. Comm. 1973, 481
55. C. Romming Acta. Chem. Scand. 1972, 26, 523
56. R. A. Bartsch, H. Chen, N. F. Haddock and P. N. Juri J. A. C. S. 1976, 98, 6753
57. R. A. Bartsch, N. F. Haddock and D. W. McCann Tetrahedron Lett. 1977, 3779
58. R. M. Izatt, J. D. Lamb, B. E. Rossiter, N. E. Izatt, J. J. Christensen and B. L. Haymore J. C. S. Chem. Comm. 1978, 386
59. R. A. Bartsch and P. N. Juri J. Org. Chem. 1980, 45, 1011
60. R. M. Izatt, J. D. Lamb, C. S. Swain, J. J. Christensen and B. L. Haymore J. A. C. S. 1980, 102, 3032
61. R. A. Bartsch and P. N. Juri Tetrahedron Lett. 1979, 407
61a. K. Laali, I. Szele and H. Zollinger Helv. Chim. Acta 1983, 66, 1737
62. M. D. Ravencroft, K. Takagi, B. Weiss and H. Zollinger Gazz. Chim. Ital. 1987, 117, 353
63. E. S. Lewis and P. G. Kotcher Tetrahedron 1969, 25, 4873
64. T. Kuokkanen Finn. Chem. Lett. 1981, 52

65. M. B. Masters Personal communication 1990.
66. S. I. Schlesinger Photogr. Sci. Eng. 1974, 18, 387
67. F. A. Cotton and G. Wilkinson "Advanced Inorganic Chemistry" Wiley Interscience 3rd Ed. 1972, P376
68. P. N. Juri and R. A. Bartsch J. Org. Chem. 1980, 45, 2028
69. B. Gloor and H. Zollinger Helv. Chim. Acta. 1971, 54, 553
70. K. F. Purcell and J. C. Kotz in "Inorganic Chemistry" Philadelphia, P. A. 1977, 270
71. J. V. Earley and T. S. Ma Mikrochim. Acta. 1960, 685
72. R. S. Bottei and N. H. Furman Anal. Chem. 1957, 29, 119
73. S. Siggia "Quantitative Organic Analysis via Functional Groups", Wiley, New York 3rd Ed., 1963, 55 and 548
74. S. Siggia "Quantitative Organic Analysis via Functional Groups", Wiley, New York 3rd Ed., 1963, 545
75. E. Bitterlin Z. Anal. Chem., 1971, 253, 120
76. R. M. Elofson, R. L. Edsberg and P. A. Mercherly J. Electrochem. Soc., 1950, 97, 166
77. R. M. Elofson and P. A. Mercherly Anal. Chem. 1949, 21, 565
78. A. Savitsky and S. Siggia Anal. Chem. 1974, 46, 149
79. E. M. Evleth and R. J. Cox J. Phys. Chem. 1967, 71, 4082
80. R. M. Elofson and F. F. Gadallah J. Org. Chem. 1969, 34, 854
81. C. Reichardt in " Molecular Interactions" Ed. H. Ratajczak and W. J. Orville-Thomas, Vol.3, Chap.5 J. Wiley. 1982.
82. U.S.P 4499170, 1985
83. K. Laali Chem Ber. 1990, 123, 1433
84. T. Kuokkannen Acta Chem. Scand. 1990, 44, 394
85. K. O. Christ e and A. E. Pavlath J. Org. Chem. 1965, 30, 3170
86. W. Ando in "The Chemistry of diazonium and diazo groups" , Ed. S. Patai, Pub. J. Wiley Chapt.9, 1978

87. D. Isac, M. Mracec, N. Prosteanu and Z. Simon Rev. Roumanian Chim., 1981, 26, 29
88. E. Scholz "Karl Fischer titration" Springer-Verlag, Berlin. Heidelberg, New York 1984
89. E. Scholz Anal. Chem. 1985, 57, 2965
90. H. Small, T. S. Stevens and W. S. Bauman Anal. Chem. 1975, 47, 1801
91. S. Siggia and J. G. Hannan "Quantitative Analysis via Functional Groups", 4th Edition, J. Wiley 1979